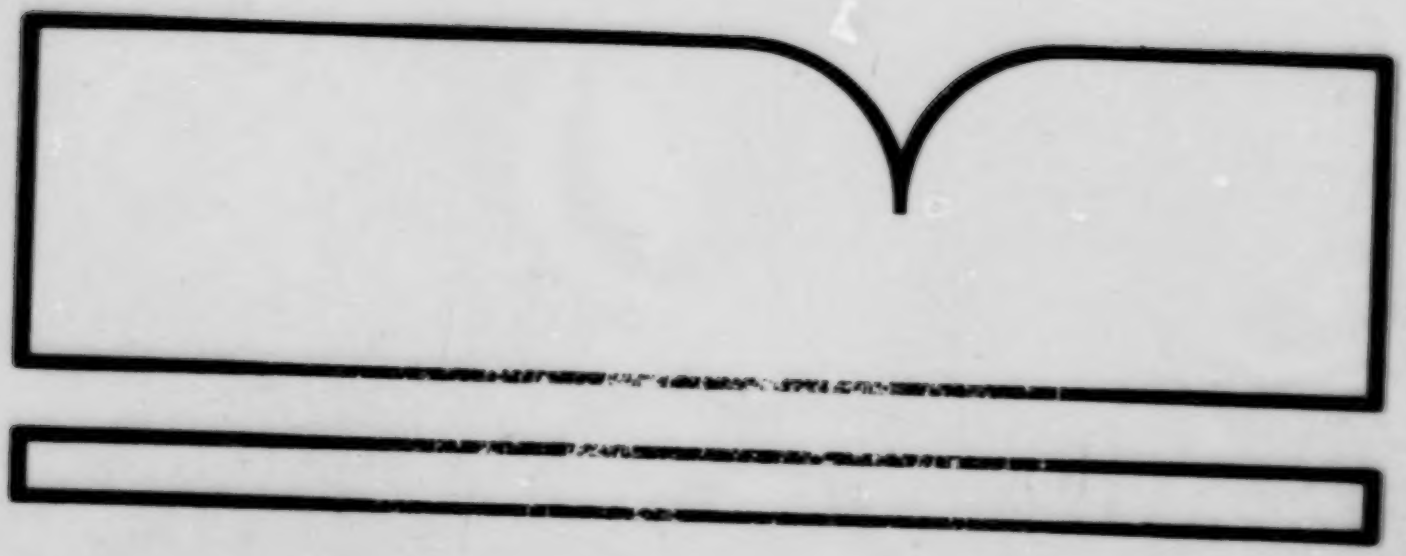
PB85-137164

# User's Guide for the Photochemical Box Model (PBM)

(U.S.) Environmental Sciences Research Lab.
Research Triangle Park, NC

Nov 84



U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Environmental Sciences Research
Laboratory
Research Triangle Park NC 27711

EPA-600/8-84-022a
November 1984

Research and Development

PB85-137164

EPA

# User's Guide for the Photochemical Box Model (PBM)

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

BIBLIOGRAPHIC INFORMATION

PB85-137164

User's Guide for the Photochemical Box Model (PBM),

Nov 84

by K. L. Schere, and K. L. Demerjian.

PERFORMER: Environmental Sciences Research Lab., Research Triangle Park, NC.
EPA/600/8-84/022A

The User's Guide for the Photochemical Box Model (PBM) attempts to describe the structure and operation of the model and its preprocessors as well as provide the potential user with guidance in setting up input data. The PBM is a simple stationary single-cell model with a variable height lid designed to provide volume-integrated hour averages of O3 and other photochemical smog pollutants of interest for an urban area for a single day of simulation. The PBM is most appropriate for application in air stagnation conditions with light and variable winds. Horizontal dimensions of the box are typically on the order of 10-50 km; the vertical dimension may vary between 0.1 and 2 km. Chemical reactions are simulated using a 63-step kinetic mechanism that includes diurnal variation of photolytic rate constants. The depth of the mixed layer also follows a diurnal pattern. The PBM assumes that emission sources are homogeneously distributed across the surface face of the box volume and that the volume is well mixed at all times. Atmospheric diffusion and wind shear are neglected. The user , ....

KEYWORDS: *Air pollution, *Mathematical models, *Photochemical box model, *Atmospheric chemistry.

Available from the National Technical Information Service, SPRINGFIELD, VA. 22161

PRICE CODE: PC A03/MF A01

EPA-600/8-84-022a

# USER'S GUIDE FOR THE PHOTOCHEMICAL BOX MODEL (PBM)

by

Kenneth L. Schere and Kenneth L. Demerjian
Meteorology and Assessment Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

## NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

## AFFILIATION

Mr. Schere and Dr. Demerjian are on assignment to the Meteorology and Assessment Division, Environmental Sciences Research Laboratory, from the National Oceanic and Atmospheric Administration, U.S. Department of Commerce.

## PREFACE

A significant area of research within the Meteorology and Assessment Division of the Environmental Sciences Research Laboratory is development, evaluation, validation, and application of models for air quality simulation, photochemistry, and meteorology. The models must be able to describe air quality and atmospheric processes affecting the dispersion of airborne pollutants on scales ranging from local to global. Within the Division, the Atmospheric Modeling Branch concentrates its activities on analytical and numerical air quality models for simulating the physical processes of transport and diffusion of pollutants in the atmosphere.

The Photochemical Box Model (PBM) is a relatively simple numerical model for simulating urban scale photochemical smog. Initial and boundary concentrations of relevant pollutant species must be provided by the user. Source emissions, wind speeds, and mixing heights must be also specified. Hourly averaged model results for $O_3$ and other species are optionally written to disk or tape for further analysis.

The first section of this user's guide is directed to managers and project directors who wish to evaluate the applicability of the model to their needs. Sections 2 and 3 are directed to engineers, meteorologists and other scientists who will be required to become familiar with the details of the model. Sections 4 and 5 are directed to persons responsible for implementing and executing the programs.

Although attempts are made to thoroughly check computer programs with a wide variety of input data, errors are occasionally found. Revisions to the model may be obtained as they are issued by completing and returning the form on the last page of this guide. Comments and suggestions regarding this publication should be directed to:

Chief, Atmospheric Modeling Branch
Meteorology and Assessment Division (MD-80)
Environmental Protection Agency
Research Triangle Park, NC 27711

For technical questions regarding use of the model, call (919)541-4524. Users within the Federal Government may call FTS 629-4524. Copies of the user's guide are available from the National Technical Information Service (NTIS), Springfield, VA 22161. A magnetic tape containing the FORTRAN source code for the PBM will be available from Computer Products, NTIS, Springfield, VA 22161. The PBM will be included in the next release (Version 6) of EPA's UNAMAP series of dispersion models.

## ABSTRACT

The User's Guide for the Photochemical Box Model (PBM) attempts to describe the structure and operation of the model and its preprocessors as well as provide the potential user with guidance in setting up input data. The PBM is a simple stationary single-cell model with a variable height lid designed to provide volume-integrated hour averages of $O_3$ and other photochemical smog pollutants of interest for an urban area for a single day of simulation. The PBM is most appropriate for application in air stagnation conditions with light and variable winds. Horizontal dimensions of the box are typically on the order of 10-50 km; the vertical dimension may vary between 0.1 and 2 km. Chemical reactions are simulated using a 63-step kinetic mechanism that includes diurnal variation of photolytic rate constants. The depth of the mixed layer, or depth of the PBM domain, also follows a diurnal pattern; it can be optionally specified as following a non-linear growth curve. The PBM assumes that emission sources are homogeneously distributed across the surface face of the box volume and that the volume is well mixed at all times. Atmospheric diffusion and wind shear are neglected.

The user must provide the PBM with initial species concentrations, hourly inputs of wind speed, source emission fluxes of CO, $NO_x$, THC, and hydrocarbon reactivity classes, and boundary species concentrations. Values of measured solar radiation and mixed layer depth may be specified at sub-hourly intervals throughout a simulation. The services of a qualified dispersion meteorologist, a chemist, and a computer programmer may be necessary to implement and apply the PBM and to interpret the results.

General information about the PBM system is contained in Section 1 of this User's Guide. A more technical description of the model and guidance for setting up input data are contained in Sections 2 and 3. Section 4 presents computer aspects of the modeling system, including an estimate of the resources needed to run the PBM. Section 5 presents an example problem.

CONTENTS


Preface ..... iii
Abstract ..... v
Figures ..... viii
Tables ..... ix

1. Overview of the PBM ..... 1
   Introduction ..... 1
   Data requirements ..... 4
   Features and limitations ..... 6

2. Technical Description of the PBM ..... 10
   Meteorology ..... 11
   Chemistry ..... 13
   Air quality and emissions ..... 19
   Numerical solution ..... 23

3. Technical Guidance for Input Data ..... 25
   Meteorological data ..... 25
   Air quality and emissions data ..... 27
   Simulation control data ..... 30

4. Computer Aspects of the PBM ..... 33
   System overview ..... 33
   Input data preparation ..... 39
   Required resources for the PBM system ..... 65

5. Example Problem ..... 67
   Description ..... 67
   Data input and program output ..... 69

References ..... 111
Appendices ..... 113

A. Considerations for using alternative chemical kinetic mechanisms ..... 113




Preceding page blank

FIGURES


| Number | | Page |
|---|---|---|
| 1 | Schematic illustration of the PBM domain | 3 |
| 2 | Normalized mixing height growth curve | 14 |
| 3 | Schematic illustration of the PBM system | 34 |
| 4 | Subroutine structure of the PBMMET preprocessor | 35 |
| 5 | Subroutine structure of the PBM | 36 |
| 6 | Input data deck setup for PBMMET | 40 |
| 7 | Input data deck setup for PBMAQE | 47 |
| 8 | Input data deck setup for the PBM | 56 |

TABLES


| Number | | Page |
|---|---|---|
| 1 | Demerjian Generalized Chemical Kinetic Mechanism | 15 |
| 2 | PBMMET Card Type 1 - Title | 41 |
| 3 | PBMMET Card Types 2, 3, and 4 - Controls | 41 |
| 4 | PBMMET Card Types 5 and 6 - Location/Units | 43 |
| 5 | PBMMET Card Type 7 - Surface Meteorological Data | 44 |
| 6 | PBMMET Card Type 8 - Solar Radiation Data | 45 |
| 7 | PBMMET Card Type 9 - Min/Max Mixing Heights | 45 |
| 8 | PBMMET Card Type 10 - Specified Mixing Heights | 46 |
| 9 | PBMAQE Card Type 1 - Title | 46 |
| 10 | PBMAQE Card Type 2 - Simulation Controls | 46 |
| 11 | PBMAQE Card Type 3 - I.C. Controls | 49 |
| 12 | PBMAQE Card Type 4 - I.C. Speciation Factors | 49 |
| 13 | PBMAQE Card Type 5 - Lateral B.C. Controls | 50 |
| 14 | PBMAQE Card Type 6 - B.C. Speciation Factors | 50 |
| 15 | PBMAQE Card Type 7 - Top B.C. Controls | 51 |
| 16 | PBMAQE Card Type 8 - Observed and Plot Species Controls | 51 |
| 17 | PBMAQE Card Type 9 - Obs. Conc. Speciation Factors | 51 |
| 18 | PBMAQE Card Type 10 and 11 - Emissions and I/O Controls | 52 |
| 19 | PBMAQE Card Type 12 - Plot Species | 53 |
| 20 | PBMAQE Card Type 13 - Initial Concentrations | 53 |
| 21 | PBMAQE Card Types 14 and 15 - Lateral Boundary Conc. | 53 |
| 22 | PBMAQE Card Types 16 and 17 - Top Boundary Conc. | 54 |
| 23 | PBMAQE Card Types 18 and 19 - Observed Concentrations | 54 |
| 24 | PBMAQE Card Types 20 and 21 - Area and Line Source Emissions | 55 |
| 25 | PBMAQE Card Types 22 and 23 - Point Source Emissions | 55 |
| 26 | PBM Card Type 1 - Title | 58 |
| 27 | PBM Card Type 2 - Options/Controls | 58 |
| 28 | PBM Card Type 3 - Print Time | 59 |
| 29 | PBM Card Type 4 - Simulation Time | 59 |
| 30 | PBM Card Type 5 - Integration Tolerance | 59 |
| 31 | PBM Card Type 6 - Update Time | 60 |
| 32 | PBM Card Type 7 - Domain Size | 60 |
| 33 | PBM Card Type 8 - Wind Speeds | 60 |
| 34 | PBM Card Type 9 - Temperatures | 61 |
| 35 | PBM Card Type 10 - Mixing Heights and Photolytic Rate Constants | 61 |
| 36 | PBM Card Type 11 - Number of Initial Species | 61 |
| 37 | PBM Card Type 12 - Initial Concentrations | 62 |
| 38 | PBM Card Type 13 - Number of Top B.C. | 62 |
| 39 | PBM Card Type 14 - Top Boundary Conc. | 62 |
| 40 | PBM Card Type 15 - Number of Lateral B.C. | 62 |
| 41 | PBM Card Type 16 - Lateral Boundary Conc. | 63 |
| 42 | PBM Card Type 17 - Number of Observed Species | 63 |
| 43 | PBM Card Type 18 - Observed Concentrations | 63 |
| 44 | PBM Card Types 19 and 20 - Emissions | 64 |
| 45 | PBM Card Types 21 and 22 - Plot Species | 64 |
| A-1 | PBM Card Type 23 - Reactions | 118 |

# SECTION 1

# OVERVIEW OF THE PBM

## INTRODUCTION

The first section of the User's Guide for the Photochemical Box Model (PBM) provides a brief description of the model system and its basis along with the general data requirements, special features, and limitations of the model. This section is intended to provide the user with adequate information to decide whether the PBM is applicable to a particular situation.

The problem of assessing and controlling urban photochemical smog has been recognized for several decades. Much has been learned about the complex chemical and physical processses involved in smog formation and transport during that time. The emissions of nitrogen oxides ($NO_x$) and reactive hydrocarbons from area, point, and line sources interact with each other and with incoming solar radiation to produce a host of intermediate and secondary chemical species in the urban atmosphere. Many of these reactions are very rapid, occurring on time scales of several seconds to several minutes. The species of greatest interest generated by photochemical smog processes is ozone ($O_3$) because of its potentially harmful effects on human health and property. Air quality simulation models aid planners and managers in making decisions to control the primary emissions ultimately responsible for producing $O_3$.

The PBM is a complex model within a simple framework. Any model that describes urban smog reactions must address the complex non-linear chemical interactions among the reacting species. These coupled non-linear reactions and the disparate time scales among the reactions preclude the use of a statistically-based (e.g.-Gaussian) linear model and necessitate a mass-con-

servative approach that usually incorporates a numerical solution to time-dependent rate equations for the chemical species. The PBM encompasses this approach within the framework of a simple single-cell domain set over the urban area of interest. The domain is a variable-volume, well-mixed reacting cell within which the physical and chemical processes responsible for photochemical smog are simulated. These include the transport and dispersion of pollutant species through the cell, the injection of primary precursor species by emissions sources, and the chemical transformation of the reactive species into intermediate and secondary products. These processes are schematically illustrated in Figure 1.

Model simulation always begins at 0500h, local standard time (LST) and continues throughout the day, typically ending at or just before sunset. Model results are provided as hour averages of all species. Instantaneous results at selected time intervals are also available. The model domain is usually chosen such that the horizontal side of the box is of fixed length from $10^1$ to $10^2$ km and such that the domain encompasses most of the major emissions sources within the urban area. Model results are averaged over the entire box volume and may not coincide with a peak concentration at a single point within the volume. For this reason the PBM may be most useful as a screening tool as an aid in deciding whether a more spatially-resolved (and resource-intensive) grid model must be applied. Also, because the box volume is fixed in space, the most appropriate meteorological conditions for application are stagnation conditions with light and variable wind conditions. Depending on the size of the box, higher winds of persistent direction may transport emitted precursor species downwind of the urban area and out of the model domain within the simulation period. A photochemical trajectory model would be more appropriate for this situation.

Earlier versions of the PBM have been used in research studies by EPA's Meteorology Division to study photochemical smog in St. Louis, MO (Schere and Demerjian, 1977) and Houston, TX (Demerjian and Schere, 1979). Also, model evaluation exercises have been conducted with the PBM for $O_3$ air quality (Shreffler and Schere, 1982; Schere and Shreffler, 1982) and for $NO_2$

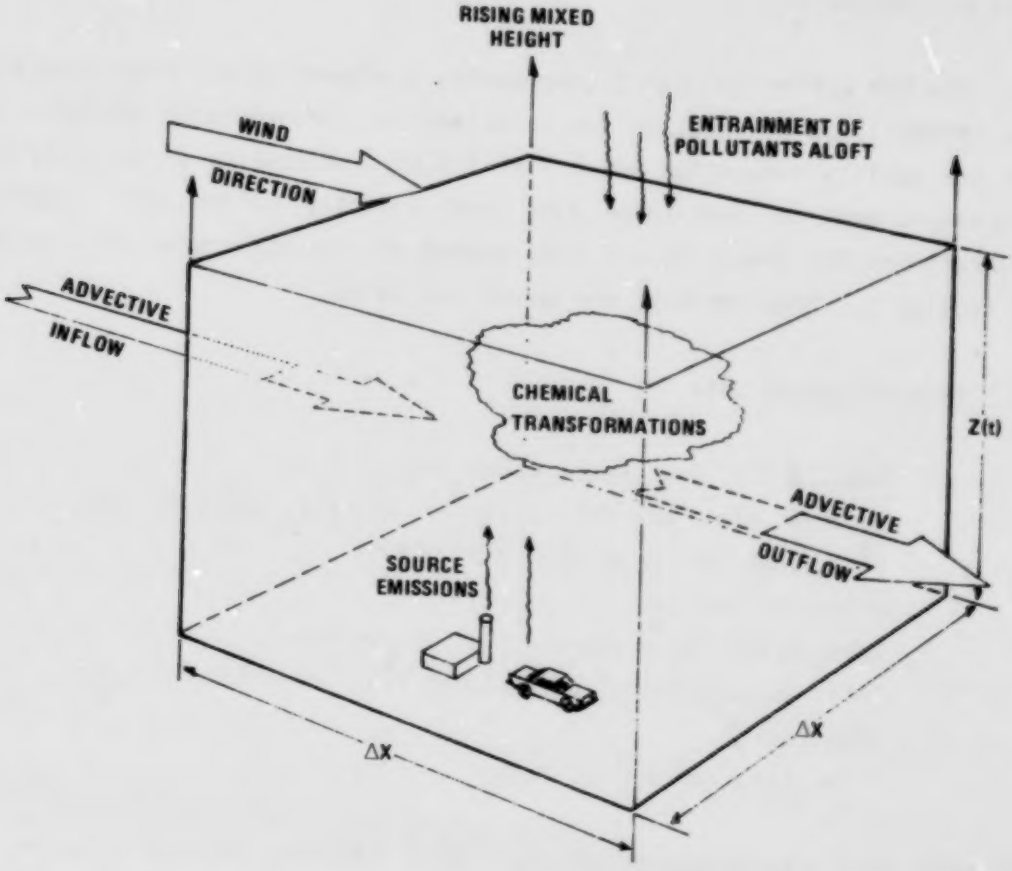



Figure 1. Schematic illustration of the PBM domain.

air quality (Schere and Shreffler, 1984) in St. Louis. The current version of the model includes several additional chemical reactions and revised reaction rate constants since the time of these earlier reports.

## DATA REQUIREMENTS

The PBM system includes 3 components: a meteorological data preprocessor (PBMMET), an air quality and emissions data preprocessor (PBMAQE), and the air quality simulation model itself (PBM). Execution of the data preprocessors sets up card-image data read directly by the PBM. Complete instructions for preparing all data needed to run the system are included in Section 3. Required data are summarized below.

Meteorological Data:

- Date (month, day, year, Julian day)
- Location (latitude and longitude, degrees, and time zone)
- Wind speed, $ms^{-1}$, knots, or $mi\ h^{-1}$
- Mixing height, m
- Ambient air temperature, °C or °F (Optional)
- Total Solar (TSR) or Ultraviolet (UV) radiation, $ly\ min^{-1}$ (Optional)
- Cloud layer amount and height, ft (Optional)

Commonly used meteorological data available from the National Climatic Center (NCC) in the form of Card Deck 144 (WBAN Hourly Surface Observations) and morning and afternoon mixing heights may be adapted as input for the PBM. However, either manual or computer processing of the NCC data will be required to scan for completeness and accuracy and to reformat the data for input to PBMMET. Use of the NCC data sets are discussed more fully in the User's Manual for CRSTER (EPA, 1977) and the Card Deck 144 WBAN Hourly Surface Observations Reference Manual (NCC, 1970).

Air Quality Data:

Initial condition concentrations, ppm
Boundary concentrations, ppm
Observed concentrations, ppm (Optional)
Hydrocarbon speciation factors for initial concentrations
Hydrocarbon speciation factors for boundary concentrations
Hydrocarbon speciation factors for observed concentrations (Optional)

Ambient concentrations of hydrocarbons in urban areas are frequently available as measures of non-methane hydrocarbons (NMHC). Since there are actually hundreds of specific compounds under this general heading, only several major structural categories or classes are chosen to simulate the range of all NMHC compounds. The speciation factors divide the gross measure of NMHC into these various categories for simulation in the air quality model.

Emissions Data:

Source emission rate of CO from area and line sources, kg $h^{-1}$
Source emission rate of CO from point sources, kg $h^{-1}$
Source emission rate of $NO_x$ from area and line sources, kg $h^{-1}$
Source emission rate of $NO_x$ from point sources, kg $h^{-1}$
Source emission rate of total hydrocarbons (THC) from area and line sources, kg $h^{-1}$
Source emission rate of THC from point sources, kg $h^{-1}$
Source emission rates of hydrocarbon classes from area and line sources, moles $h^{-1}$
Source emission rates of hydrocarbon classes from point sources, moles $h^{-1}$
Ratio of $NO_2/NO_x$ in area and line source $NO_x$ emissions
Ratio of $NO_2/NO_x$ in point source $NO_x$ emissions
Ratio of $CH_4$/THC in area and line source THC emissions
Ratio of $CH_4$/THC in point source THC emissions

Control Data:

Horizontal side of model domain, km
Number of hours of simulation
Time interval for printing and plotting instantaneous concentrations, min
Time interval for updating mixing height and photolytic rate constants, min
Numerical integration tolerance parameter
Values for selecting specific options

## FEATURES AND LIMITATIONS

Several specific features of the PBM system are highlighted below. Also, the major assumptions invoked in the model's formulation and some of its limitations are explained.

The special features include:

(1) Mixing Height Growth - The PBM includes an option to interpolate between minimum and maximum specified mixing heights in a non-linear manner characteristic of the true growth rate in sunny, low-wind conditions ('characteristic curve').

(2) Photolytic Rate Constants - PBMMET generates values for the diurnal variation of the photolytic rate constants required for the photolysis reactions in the chemical kinetic mechanism. These rate constants are calculated from a theoretical clear-sky perspective with options to attenuate the values based on observed cloud conditions or measured solar radiation. These rate constants may be generated for the surface layer or as an integrated average through the depth of the mixed layer.

(3) Modular Chemical Kinetics - The default chemical kinetic mechanism in the PBM models the reactions of the HC-$NO_x$-$O_3$ urban photochemical smog system. It contains 63 reactions and 41 individual chemical species with 8 classes of hydrocarbons. The kinetics are modular and may be replaced with another mechanism with relatively few coding changes required by the user.

(4) Numerical Solution Scheme - A modified version of the Gear (1971) numerical solution technique is used to solve the coupled differential species rate equations. The solution scheme is very accurate and no steady-state approximations are needed.

The major assumptions contained in the PBM formulation include:

(1) The box volume is well mixed at all times and no spatial variations of concentration occur within it.

(2) Emissions sources are homogeneously distributed across the surface face of the box volume.

(3) Entrainment of outside air occurs laterally by advective transport and vertically by the rising mixed layer.

(4) Molecular and atmospheric diffusion are neglected.

(5) Horizontal and vertical wind shear are neglected.

These assumptions must be considered before applying the PBM to a particular situation. If, for example, the vast majority of hydrocarbons are emitted into the urban atmosphere from a single point source located near an edge of the domain, assumption (2) is probably violated and the model would not be appropriate for the application.

Care should be exercised in choosing the size and location of the PBM modeling domain for a given application. Because the domain is fixed in space, the locations of ambient monitoring stations and the spatial distribution of source emissions will aid in choosing the position of the domain. Major area and line sources within the urban area should be within the domain. Significant land areas without area or line sources should not be within the domain. Point sources should also be included within the domain to the extent that they are within an otherwise distributed emissions area and are not isolated outside of the area of interest. The following are rough guidelines for choosing the size of the horizontal side of the domain:

| | |
|---|---|
| Small cities (population 10,000-100,000): | 5-15 km |
| Medium cities (population 100,000-500,000): | 15-30 km |
| Large cities (population >500,000): | 30-50 km |

The exact size for a particular application should be determined more by the spatial distribution of emissions and population rather than by the overall population. For very large cities distributed over considerable distances, the model domain may have to focus only on a portion of the urban area. Because the PBM is most aptly used in stagnation conditions, wind speeds are not a major factor in determining the domain size. The domain that is finally chosen should include at least one meteorological and air quality monitoring site that is representative of the area being modeled. Also, an upwind monitoring location outside of the domain is needed to provide boundary conditions.

The PBM is not applicable to the regional scale (500-1000 km) oxidant problem. Considerations of spatial inhomogeneities, large-scale meteorological processes, and multi-day chemistry that includes slow reactions preclude use of the simplistic modeling framework of the PBM. Lamb (1983) discusses some of the special needs in regional photochemical modeling and presents a framework for such a model.

Finally, the PBM provides a measure of air quality averaged over the entire volume of the domain. It does not show "hotspots" or single sites of National Ambient Air Quality Standards (NAAQS) exceedance. However, if the PBM application shows the volume-average concentration of $O_3$, for instance, to be in excess of the NAAQS, use of a more sophisticated model to help identify hotspots may be required.

## SECTION 2

## TECHNICAL DESCRIPTION OF THE PBM

The basic equation underlying the PBM is the atmospheric diffusion equation, simplified as a result of the assumptions listed in the previous section:

$$\frac{\partial \bar{c}_i}{\partial t} = \bar{u}\frac{\partial \bar{c}_i}{\partial x} + \frac{\partial z}{\partial t}\frac{\partial \bar{c}_i}{\partial z} + \frac{\bar{Q}_i}{z} + R_i(\bar{c}_i,\ldots,\bar{c}_n) \qquad (1)$$

where $\bar{c}_i$ = mean concentration of species i within the PBM domain,

$\bar{u}$ = mean wind speed within the domain,

$\bar{Q}_i$ = source emissions flux (mass time$^{-1}$ length$^{-2}$) of species i into the domain,

$R_i$ = rate of production and/or destruction of species i from chemical species,

$x,z,t$ = length and time variables.

This equation embodies the principle of conservation of mass; it is solved numerically within the PBM for the concentrations $c_i$ as a function of time. Hour-averaged concentrations are then formed. This section of the User's Guide discusses technical aspects of this formulation as implemented in the PBM system.

## METEOROLOGY

The PBM requires values of specific meteorological parameters in order to solve Equation (1). These include hourly values of the wind speed $\bar{u}$, subhourly values of the mixing height growth $\partial z/\partial t$ and, optionally, solar radiation or observed cloud heights and amounts. Hourly ambient temperatures may also be required. These parameters are all processed by PBMMET, the meteorological preprocessor. Since the solar radiation and temperature values as well as the cloud parameters pertain to the calculation of chemical reaction rate constants, they will be discussed within the subsection on chemistry.

Ideally, the winds input to the model should be averaged through the depth of the mixed layer. Where such vertically resolved data are available they should be used. Otherwise, a representative sampling of surface wind speeds within the PBM domain will suffice. Wind speeds are needed within the PBM to help determine the advective transport term $\bar{u}\,\partial\bar{c}_i/\partial x$, providing a horizontal dilution rate of material within the box volume and entrainment from the upwind side. As mentioned previously, the PBM is most applicable under stagnation conditions where the wind speeds are light (generally under 2 $ms^{-1}$) and directions are variable. Winds with more persistent directions may also be used in the PBM, although the area of greatest interest for photochemical pollutant species may well be downwind of the box volume in this case.

Concentration predictions from the PBM are sensitive to changes in the volume of the modeling domain. It is therefore important to accurately specify the growth rate of the mixing height, $\partial z/\partial t$, since this term controls the vertical dilution and entrainment. Historically it has been frequent practice to linearly interpolate between the mixing height determined from a morning temperature sounding and an afternoon mixing height determined from a combination of sounding measurements and principles of atmospheric thermodynamics. The problem with this method is that the linear interpolation tends to overestimate the depth of the mixed layer at

early times and to underestimate later. This error in the mixed layer depth, and hence in $\partial z/\partial t$, can introduce serious errors in the model predictions of pollutant species concentrations.

In an effort to produce a more realistic interpolation between morning minimum and afternoon maximum mixed layer depths, the following characteristic curve was developed along the lines of actual observed growth rates in clear sky, light wind conditions. If G represents the growth of the mixed layer (afternoon maximum depth minus morning minimum depth), and DL represents the day length or length of time between sunrise and sunset, the following points are postulated:

$$
\begin{aligned}
&Z(SR)=HMIN_0 \\
&Z(SR+0.07DL)=HMIN_0 + 0.02G \\
&Z(SR+0.14DL)=HMIN_0 + 0.10G \\
&Z(SR+0.33DL)=HMIN_0 + 0.58G \\
&Z(SR+0.50DL)=HMIN_0 + 0.85G \\
&Z(SR+0.70DL)=HMAX
\end{aligned}
\qquad (2)
$$

where Z is the mixed layer depth, $HMIN_0$ and HMAX are the morning minimum and afternoon maximum depths, and SR is the time of sunrise. These node points represent percentages of the total growth occurring within corresponding percentages of elapsed daylight time. Intermediate depths are interpolated by cubic splines as often as every 10 minutes for frequent updates within the PBM. This produces smooth variations in $\partial z/\partial t$ during the period of fastest growth in the mixed layer depth. Beyond this time the following points are postulated:

$$
\begin{aligned}
&Z(SR+0.90DL)=HMAX \\
&Z(SS)=HMIN_0+0.50G \\
&Z(SS+0.50NL)=HMIN_1
\end{aligned}
\qquad (3)
$$

where $HMIN_1$ is the following morning minimum depth, SS is the time of sunset,

and NL is the length of time between sunset and the following sunrise. The specification of these points accounts for the rapid drop in mixed layer depth as the surface layer becomes decoupled from the layer aloft when surface stabilities increase near sunset. Interpolation between the points shown by Equation set (3) is linear. Figure 2 shows the pattern of mixed layer growth (until time SS taken from Equation sets (2) and (3)) occurring during a typical PBM simulation period. Mixing depths and times have been normalized to HMAX and DL, respectively.

Alternatively, the PBM user may directly set up mixed layer height values for input to the PBM at subhourly intervals. Linear interpolation will be performed between input values if needed.

## CHEMISTRY

The PBM contains a 63-step chemical kinetic mechanism, shown in Table 1, developed by Dr. Kenneth Demerjian of EPA. The reactions include 37 reactive species and 8 hydrocarbon classes. In Equation (1), the term representing the chemical interactions, $R_i(c_i,....,c_n)$, implies that the rate of change of species i is not only dependent upon the concentration of species i but also upon the concentrations of n other species. In this way the reaction set is coupled between species. Solution of the resulting set of 37 nonlinear differential equations is performed numerically by finite differences.

Most chemical kinetic mechanisms that simulate urban photochemical smog treat the relevant inorganic chemical reactions similarly. Differences between the mechanisms occur most often in the handling of the organic species chemistry where hundreds of different reactive hydrocarbon compounds have a role in the photochemical cycle. Limiting the number of these compounds in a kinetic mechanism requires the use of assumptions and approximations. The Demerjian mechanism uses the technique of generalized species lumping, in which an entire group of compounds is represented by a generalized species, the chemistry of which reflects the common features of that entire group. The rate constants for reactions that include these lumped groups, or

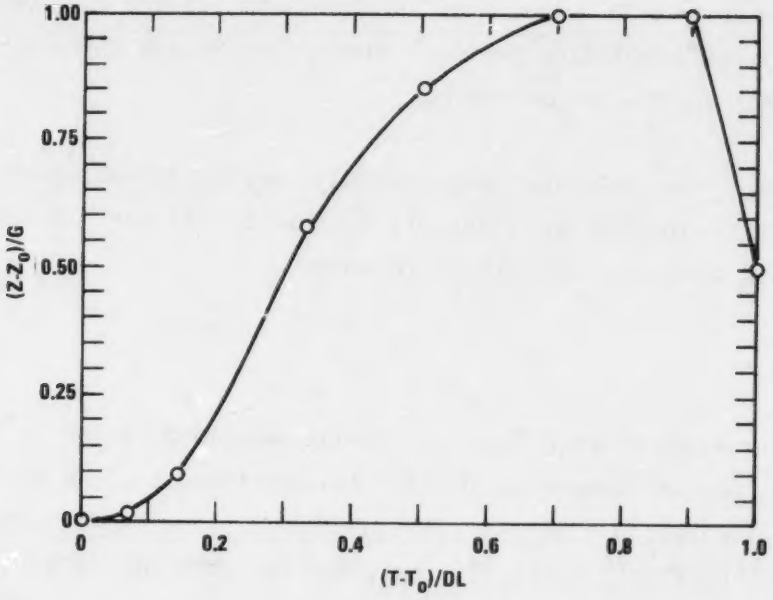



Figure 2. Normalized mixing height growth curve. $T_0$, $Z_0$ represents the time and mixing height at sunrise. DL, G represents the time between sunrise and sunset and the total mixing height growth.

TABLE 1. DEMERJIAN GENERALIZED CHEMICAL KINETIC MECHANISM.

| REACTION NUMBER | REACTION | RATE CONSTANT (Units[a]) |
|---|---|---|
| 1 | NO2 + hν ----> NO + O | 4.80E-01[b,d] |
| 2 | O + O2 + M ----> O3 + M | 2.25E-05[c] |
| 3 | O3 + NO ----> NO2 + O2 | 2.68E+01 |
| 4 | O3 + NO2 ----> NO3 + O2 | 4.76E-02 |
| 5 | O3 + hν ----> O1D + O2 | 1.96E-03[b,d] |
| 6 | O1D + M ----> O + M | 4.23E+04 |
| 7 | O1D + H2O ----> 2.00HO | 3.40E+05 |
| 8 | NO3 + NO ----> 2.00NO2 | 2.96E+04 |
| 9 | NO3 + NO2 ----> N2O5 | 1.78E+03 |
| 10 | N2O5 ----> NO3 + NO2 | 3.11E+00[b] |
| 11 | N2O5 + H2O ----> 2.00HNO3 | 1.92E-05 |
| 12 | HONO + hν ----> HO + NO | 9.58E-02[b,d] |
| 13 | HO + CO ----> HO2 + CO2 | 4.14E+02 |
| 14 | HO2 + NO2 ----> HONO + O2 | 4.40E+00 |
| 15 | HO2 + NO ----> HO + NO2 | 1.22E+04 |
| 16 | HO2 + NO2 + M ----> HO4N + M | 1.52E-03[c] |
| 17 | HO4N ----> HO2 + NO2 | 3.26E+00[b] |
| 18 | HO + HONO ----> NO2 + H2O | 9.75E+03 |
| 19 | HO + NO2 + M ----> HNO3 + M | 1.43E-02[c] |
| 20 | HO + NO + M ----> HONO + M | 7.35E-03[c] |
| 21 | HO + HNO3 ----> H2O + NO3 | 1.97E+02 |
| 22 | HO2 + O3 ----> HO + 2.00O2 | 2.96E+00 |
| 23 | HO + O3 ----> HO2 + O2 | 1.01E+02 |
| 24 | HO2 + HO2 ----> H2O2 + O2 | 3.73E+03 |
| 25 | H2O2 + hν ----> 2.00HO | 4.21E-04[b,d] |
| 26 | ETH + O3 ----> 0.40RO2 + FORM + 0.10HO2 | 2.50E-03 |
| 27 | ETH + HO ----> FRO2 + FORM | 1.20E+04 |
| 28 | OLE + O ----> RO2 + ALD + HO2 | 5.10E+03 |
| 29 | OLE + O3 ----> 0.75RO2 + 0.75ALD + 0.40HO2 | 9.50E-02 |
| 30 | OLE + HO ----> RO2 + 0.75ALD + 0.25FORM | 5.50E+04 |
| 31 | PAR + HO ----> RO2 | 5.00E+03 |
| 32 | FORM + hν ----> CO | 2.36E-05[b,d] |
| 33 | FORM + hν ----> 2.00HO2 + CO | 1.62E-03[b,d] |
| 34 | FORM + HO ----> HO2 + H2O + CO | 1.60E+04 |
| 35 | RO2 + NO ----> RO + NO2 | 1.10E+04 |
| 36 | RO + O2 ----> 0.75ALD + HO2 + 0.25FORM | 8.99E-01 |
| 37 | ALD + hν ----> RO2 + HO2 + CO | 3.79E-04[b,d] |
| 38 | ALD + HO ----> R1O2 + H2O | 2.40E+04 |
| 39 | FRO2 + NO ----> FRO + NO2 | 1.10E+04 |
| 40 | FRO + O2 ----> FORM + HO2 | 1.08E+00 |
| 41 | R1O2 + NO2 ----> PAN | 8.87E+03 |
| 42 | PAN ----> R1O2 + NO2 | 1.35E-01[b] |
| 43 | RO + NO2 ----> RNO3 | 1.00E+02 |

(continued)

TABLE 1. (CONTINUED)

| REACTION NUMBER | REACTION | RATE CONSTANT (Units[a]) |
|---|---|---|
| 44 | R02 + 03 ----> R0 + 2.0002 | 2.00E+00 |
| 45 | R102 + NO ----> R02 + NO2 | 2.07E+04 |
| 46 | TOL + HO ----> RT02 + ALD + DCB1 | 8.70E+03 |
| 47 | ARO + HO ----> RX02 + ALD + DCB1 | 3.40E+04 |
| 48 | RT02 + NO ----> RTO + NO2 | 1.10E+04 |
| 49 | RTO + 02 ----> DCB1 + H02 + CO | 8.87E-01 |
| 50 | RX02 + NO ----> RXO + NO2 | 1.10E+04 |
| 51 | RXO + 02 ----> DCB2 + H02 + CO | 8.87E-01 |
| 52 | DCB1 + hν ----> 2.00CO + 2.00H02 | 1.92E-03[b,d] |
| 53 | DCB1 + hν ----> 0.20FORM + 1.80CO | 1.92E-03[b,d] |
| 54 | DCB1 + HO ----> H02 + 2.00CO | 1.70E+04 |
| 55 | DCB2 + hν ----> R102 + H02 + 2.00CO | 4.56E-03[b,d] |
| 56 | DCB2 + hν ----> 0.50ALD + 0.50FORM + 0.50FR02 | 4.56E-03[b,d] |
| 57 | DCB2 + HO ----> R102 + CO | 2.56E+04 |
| 58 | RT02 + 03 ----> RTO + 2.0002 | 2.00E+00 |
| 59 | RX02 + 03 ----> RXO + 2.0002 | 2.00E+00 |
| 60 | R102 + 03 ----> R02 + 2.0002 | 2.00E+00 |
| 61 | OLE + 03 ----> COOH + ALD | 1.50E-03 |
| 62 | NMHC ----> | 0.00E+00[b] |
| 63 | NONR ----> | 0.00E+00[b] |

a Rate constant units are $ppm^{-1}$ $min^{-1}$ unless otherwise noted
b Units of rate constant are $min^{-1}$
c Units of rate constant are $ppm^{-2}$ $min^{-1}$
d Photolysis rate constant - Value shown is for clear-sky conditions, a solar zenith angle of 40 degrees, and integrated through a 1 km deep mixed layer

reactivity classes, should be calculated as averages of the rate constants for the reactions that involve the individual compounds within the given reactivity class.

An earlier version of the mechanism used in the PBM is described in McRae et al. (1983). This earlier version and the current version include the lumped hydrocarbon classes of non-reactives, olefins, paraffins, aldehydes, and aromatics. In the current version, however, several species have been separated from these generalized classes to be treated explicitly within the mechanism either because of significant reactivity differences or product distributions different from the mainstream of the class. These species include ethylene (separated from the olefins), toluene (separated from the aromatics), and formaldehyde (separated from the aldehydes). In addition, the photolysis of the dicarbonyls, predominantly glyoxal and methylglyoxal, was included in the current version. Separate reaction pathways for the new species were included in the mechanism. Reaction rate constants used are current literature values, and where ambient temperature changes may significantly affect these values the full temperature-dependent expressions are used to compute them.

Predicted concentrations of NMHC (ppmC) can not be simply formed from the sum of the predictions of the concentrations of the individual hydrocarbon classes (ppm). Therefore, the concentrations of ambient NMHC produced by the PBM using the Demerjian kinetic mechanism are estimates based on emissions, transport and dilution. Predicted NMHC concentrations are therefore only approximations. They should be most accurate when emissions and dilution are dominant processes, such as in the first few hours of simulation, or when transport is dominant.

The chemical kinetic mechanism requires that the photolytic rate constants for $NO_2$, $O_3$--> O('D), HONO, $H_2O_2$, formaldehyde (into molecular products), formaldehyde (into radical products), acetaldehyde (into radical products), and the dicarbonyl species glyoxal and methylglyoxal be speci-

fied. These rate constants correspond to reactions 1, 5, 12, 25, 32, 33, 37, 52, 53, 55, and 56, respectively, of the default kinetic mechanism (Table 1). Two photolysis reactions for each of the dicarbonyl species are shown. The photolytic rate constants are directly proportional to the amount of solar radiation received and, thus, vary over a diurnal cycle which changes with season and geographical location. While clear-sky and totally overcast days show smoothly varying functions of solar radiation, partly cloudy days are often characterized by more rapid fluctuations. Because the entire reaction mechanism is perturbed by the changes in the photolytic rate constants they are frequently updated during model simulation.

There are significant vertical variations in the values of some of the photolytic rate constants within the lowest 1-2 km of the atmosphere. A problem arises as to the choice of a vertical level for values of the photolytic rate constants because the PBM does not permit vertical resolution in its structure. The meteorological preprocessor, PBMMET, provides the user with a choice of surface-level rate constants or rate constants averaged through the depth of the mixed layer at any point in time. These two methods serve as lower and upper bounds on the probable value of the photolytic rate constants.

The rates at which a particular species photolyzes are dependent upon the particular wavelength band of radiation the species is sensitive to, the amount of radiation received within this band, the efficiency with which the species absorbs the radiation, and the yield of product species per unit of absorbed radiation. Demerjian et al. (1980) discuss the theoretical considerations involved in calculating photolytic rate constants for many species of interest to air pollution analysts and tabulate values of the rate constants over a range of zenith angles and vertical levels for clear-sky conditions. PBMMET uses these values, with some updates since the time of the article's publication, to generate surface-level or layer-averaged values of photolytic rate constants.

In real atmospheric situations, conditions often vary from clear skies. The clear sky theoretical rate constants may be reduced by an attenuation

factor to account for the presence of clouds or other obscuring phenomena. This factor may be determined from measured values of solar radiation, either in the ultraviolet or total solar bands, or from cloud cover and height observations. For the case of measured radiation, the attenuation factor is formed from a ratio of the empirically determined surface layer value of the $NO_2$ photolysis rate constant (from radiation measurements) to the clear-sky theoretically determined value of the same parameter. For the case of cloud cover observations, the method of Jones et al. (1981) was used to calculate attenuation factors. These authors calculated the attenuation factors corresponding to various cloud amounts and heights (commonly reported from National Weather Service (NWS) observations) from empirical relationships based on measured $NO_2$ photolysis data.

Many of the remaining non-photolytic reactions in the chemical kinetic mechanism have rate constant values that are sensitive to temperature. When available, hourly ambient temperatures may be input to the PBM to adjust the temperature-dependent rate constants. This is done once for each hour of simulation for each such reaction. In the absence of input temperatures all temperature-dependent rate constants are calculated for 298°K ( ~77°F).

## AIR QUALITY AND EMISSIONS

Air quality observations are required to compute values for certain $\bar{c}_i$'s in Equation (1). In particular, initial conditions are needed for the $\partial\bar{c}_i/\partial t$ term, lateral inflow boundary conditions for $\partial\bar{c}_i/\partial x$, and boundary conditions at the top of the model domain for $\partial\bar{c}_i/\partial z$. Also, air quality observations may be used to verify the results of the PBM simulation.

It is important to attempt to specify the initial species concentrations as accurately as possible because they determine the amount of mass with which the reactive system begins the simulation. Until the emissions terms have introduced sufficient mass into the system the simulation can be dominated by the initial condition specifications. At least one, and preferably several, air quality monitoring stations should be within the

bounds of the model domain. Their average should provide a representative sampling of conditions within the area being modeled. Initial conditions existing at model simulation starttime (0500h, LST) must be specified for CO, NO, $NO_2$, and NMHC. The intermediate and termination species concentrations need not be specified.

A critical element in specifying initial conditions is apportioning the hydrocarbon concentration among the various organic reactivity classes. For the default chemical kinetic mechanism these include non-reactives (NONR), ethylene (ETH), olefins or all alkenes except ethylene (OLE), paraffins or all alkanes other than methane (PAR), formaldehyde (FORM), all other aldehyde species (ALD), toluene (TOL), and all other aromatic species (ARO). The preferred method for determining this apportionment is from a detailed analysis of a gas chromatograph-mass spectrometer (GC/MS) profile of the particular organic compounds and their fractional weights within a captured air sample taken in the urban area modeled during the period 0600-0900h, LST. These compounds and their weights are then assigned to the various reactivity classes; sums of each class are then calculated and proportional splitting factors are determined. McRae et al. (1983) provide a detailed example of how this apportionment is done using a detailed GC/MS analysis from a smog chamber air sample and 6 different chemical kinetic mechanisms. Alternatively, an option is available to the user of utilizing the urban splitting factors developed by the authors for application of the PBM to St. Louis. These factors are presented in Section 4 of the user's guide and are applied to the measured NMHC initial condition. The risk in using these factors is that the relative weighting of the reactivity classes in the user's area of application may be different from those in St. Louis. This is especially true for cities where the relative distribution of mobile and stationary sources differs appreciably from St. Louis.

Hourly values of upwind boundary species concentrations are also required for each hour of simulation. At least one monitoring station should be available for determining boundary concentrations of CO, NO, $NO_2$, NMHC, and $O_3$. Boundary concentrations for the speciated hydrocarbon classes

are also required. As in the case of initial conditions, the preferred method for determining the splits between these classes is from a GC/MS analysis of upwind sampled air. Alternatively, the same splitting factors developed for the initial conditions may be applied to the boundary concentrations. The inherent problem in this approach is that the reactive splits of the more aged air moving into the urban area at the upwind boundary may be different from those representing urban air laden with fresh reactive organic emissions. In the absence of any analyzed samples the default factors for St. Louis may be used with the caution expressed above for default initial conditions. The PBM contains an option to calculate the upwind $O_3$ concentration from the given upwind NO and $NO_2$ concentrations and photostationary state assumptions. This is advisable when upwind $O_3$ measurements are not available, but NO and $NO_2$ are. Where upwind $O_3$ observations exist, they should be used. The relative importance of boundary conditions to the air quality simulation increases as wind speed increases.

In addition to lateral boundary conditions, hourly boundary concentrations at the top of the model domain may be input. If vertical profiles of species concentrations exist for the urban area, the top boundary concentrations may be determined from them. Without such profiles, tropospheric background concentrations may be assumed. Frequently, there is a significant concentration of $O_3$ aloft that is entrained into the rising mixing layer during the growth period. A technique is presented in Section 3 for estimating the $O_3$ concentration aloft at the top of the modeling domain in the absence of measured $O_3$ profiles.

Optionally, hourly concentrations of measured species within the PBM domain may be specified for comparison with model predictions. These observed concentrations are output by the PBM on time series plots and written off to disk/tape storage for later use in statistical analysis of model results. If desired, splitting factors for the observed hydrocarbon species may be specified here also, or the default factors can be used. Preparation of all air quality data for the PBM is handled by the air quality and emissions preprocessor, PBMAQE.

Source emissions are also prepared by PBMAQE for input to the PBM. For primary pollutant species i, source emissions enter the model formulation shown in Equation (1) through the flux term $\overline{Q}_i/z$.

The spatial and temporal variation in primary pollutant sources is a major influence for air pollutant patterns in a region. Temporal resolution of sources is an important parameter within the PBM; spatial resolution is not of concern because of the assumption of spatial homogeneity of sources. The PBM accepts hourly source emission rates that encompass the sum of all sources within the modeling domain. In reality, emissions originate from one of three distinct types of source configurations: area, line, or point. Although line sources, principally roadways, are not treated explictly by the PBM, they represent a major portion of the total emissions of primary reactive species emanating from an urban area. The temporal resolution of the line sources is apt to contain more structure than that of the other source types because of a twin-peaked diurnal traffic pattern. Some knowledge of this pattern for a potential modeling site is essential in order to form a representative temporal emissions pattern from the mobile sources. Point sources are not treated separately by the PBM. Total hourly emission rates from all point sources are calculated and added to the hourly rates from area and line sources to form a single emissions rate for each hour for each primary species.

The PBM requires partitioning of nitrogen oxides ($NO_x$) and total hydrocarbon (THC) emissions into their respective chemical components for the default chemical kinetic mechanism. Source emissions of $NO_x$ are subdivided between the constituent species NO and $NO_2$. Estimates of $NO_2/NO_x$ in auto exhaust tailpipe emissions range from 3 to 5%. However, there is a rapid period of thermal oxidation of NO to $NO_2$ due to Reaction (4) occurring in the early stages of exhaust dilution.

$$2NO+O_2 \rightarrow 2NO_2 \qquad (4)$$

The implicit consideration of this process in the model leads to the estimate of $NO_2/NO_x \approx 10\%$ for primary emissions of $NO_x$.

Hydrocarbon emissions are generally reported as THC and must be distributed among the reactive organic classes required by the generalized kinetic mechanism. This is accomplished through an approach similar to that outlined by Bucon et al. (1978), in which distributions are derived based on hydrocarbon composition analysis by source emissions processes. The splits between the various hydrocarbon classes: NONR, ETH, OLE, PAR, FORM, ALD, ARO, and TOL will vary with the distribution of source types in a given modeling domain. A concentration of petroleum refineries and storage tank facilities in a particular area, for instance, would cause the hydrocarbon distribution to differ from that found in a non-industrial metropolitan area with heavy automobile traffic.

Emission rates are typically reported as mass of material within a set time interval, such as kg $h^{-1}$. PBMAQE accepts emissions in these units for the species CO, $NO_x$, and THC. These emission rates along with the horizontal size of the model domain, ambient temperature, and molecular weight of the emitted species allow PBMAQE to compute corresponding volumetric flux rates for the PBM. Emission rates of the reactive organic classes are reported as moles/hr, according to the procedure of Bucon et al. (1978).

## NUMERICAL SOLUTION

Each reactive species included in the chemical kinetic mechanism is represented in the model by a differential equation such as Equation (1). The equilibrium time constants among the various reactions can vary by orders of magnitude; this variation makes the system of equations "stiff" and difficult to solve by conventional numerical techniques used for ordinary differential equations. The technique chosen for the PBM is a modified version of Gear's method (1971), a variable-order method based on a backward differentiation multistep formula. Because the chemistry has the most stringent step size requirements of any of the components in the PBM, it is the

rate-controlling step for the entire model. The Gear routine begins with a very small time step and subsequently adjusts the step size upward while concurrently seeking to maintain the solution within all specified tolerances. Concentrations of all simulated species are computed in this manner. Steady-state approximations are not invoked here, as the efficiency of the numerical solution obviates the need for such computationally time saving measures. Moreover, such approximations may introduce large numerical errors into the solution (Farrow and Edelson, 1974).

# SECTION 3

# TECHNICAL GUIDANCE FOR INPUT DATA

Section 4 of this user's guide provides a detailed description of the structure and format of the data needed to run the PBM and its preprocessors. The identification of many of the data items there will be sufficient description for users to correctly choose values. However,an expanded description, with guidance for making decisions on values for the data, is necessary for some of the input data items. This section provides these descriptions and guidance where necessary. Unless otherwise indicated, values for data input items should be volume averaged over the PBM domain.

## METEOROLOGICAL DATA

### Mixing Heights

The meteorological preprocessor, PBMMET, offers the user several options for choosing mixing height values to be input to the PBM. The major choice is between direct specification of the mixing heights or interpolation between the morning minimum and afternoon maximum heights via the characteristic curve method. Where detailed vertical temperature soundings are available more frequently than the usual twice daily NWS profile, the user may be able to accurately determine the temporal variation of mixing heights. When this is the case, the direct input method should be chosen with an input time increment as small as possible, but no larger than 60 minutes. The characteristic curve method should be used in other situations. The morning minimum mixing height (and the next morning's minimum) can usually be determined from the 12Z sounding at the closest NWS rawinsonde location. If this location is not representative of the urban terrain and

displays a surface-based temperature inversion, a minimum default value of 100 m above ground level (agl) for 0500h, LST should be input to account for the urban influence. In no case should a specified or interpolated mixing height value be less than 100 m, agl. The afternoon mixing height depth may be determined either from the 00Z NWS sounding or from the maximum afternoon surface temperature and the morning sounding (Holzworth, 1972). The maximum specified mixing height should not exceed 2000 m, agl. Daily minimum and maximum mixed layer depths for NWS rawinsonde sites are also available from the NCC.

## Photolytic Rate Constants

A number of choices must be made concerning the calculation method of the photolytic rate constants. The first is whether to use surface-based or mixed-layer average rate constants. This is an important decision because there can be substantial vertical variation in the values of the photolytic rate constants in the lowest 1-2 km of the atmosphere; PBM results for $O_3$ are sensitive to these rate constants. For a single simulation, the layer-average method should be used to produce an upper bound on model results. However, if resources permit, a second simulation using surface-based rate constants may be conducted in order to determine the lower bound, and hence the probable range, of predicted concentrations based on the expected variations in the photolytic rate constant values.

A choice of clear-sky or attenuated photolytic rate constants is also available. In the absence of sufficient observations of solar radiation or cloud amounts and heights, the clear-sky method should be chosen. This method is also most applicable for determining the maximum potential $O_3$ generated by the given emissions and ventilation conditions within an urban area. If attenuated rate constants are desired, the attenuation factors may be determined based on continuously monitored UV solar radiation (wavelengths less than 3850 A), continuously monitored TSR, or hourly NCC cloud layer reports of amount and height. When the radiation data are available, they should be specified in units of langleys $min^{-1}$, at

intervals as small as possible, but not less than 10 min or more than 60 min. A value of 10 min is recommended. Also, if mixing heights or solar radiation values are directly input to PBMMET, the time increment at which these values are specified should not be less than the time increment for outputs from PBMMET.

AIR QUALITY AND EMISSIONS DATA

Speciation Factors for Ambient NMHC

Initial condition and, optionally, boundary condition and observed values of NMHC concentrations must be subdivided into 8 hydrocarbon reactivity classes. The air quality and emissions preprocessor, PBMAQE, allows the user to specify the factors with which to perform this operation. The specific reactivity classes include NONR, ETH, OLE, PAR, FORM, ALD, ARO, and TOL.

Laboratory analysis of captured ambient air samples can help determine the splitting factors. A detailed example of this procedure is illustrated in McRae et al. (1983) for an earlier version of the Demerjian (default) chemical kinetic mechanism reactivity classes. The current version of the mechanism has similar classes, except that ethylene is split from other olefins, formaldehyde is split from other aldehydes, and toluene is split from other aromatics. This modification is easily incorporated into the procedure illustrated in the McRae reference.

If detailed analyses of ambient air samples are not available, the user has the option to choose the default values provided by PBMAQE. These values were determined for the PBM application to the St. Louis, MO area. They are presented below in Equation set (5).

$$
\begin{aligned}
\text{NONR (ppm)} &= 0.0440\ \text{NMHC (ppmC)} \\
\text{ETH (ppm)} &= 0.0263\ \text{NMHC (ppmC)} \\
\text{OLE (ppm)} &= 0.0394\ \text{NMHC (ppmC)} \\
\text{PAR (ppm)} &= 0.0786\ \text{NMHC (ppmC)} \\
\text{FORM (ppm)} &= 0.0608\ \text{NMHC (ppmC)} \\
\text{ALD (ppm)} &= 0.0202\ \text{NMHC (ppmC)} \\
\text{ARO (ppm)} &= 0.0149\ \text{NMHC (ppmC)} \\
\text{TOL (ppm)} &= 0.0099\ \text{NMHC (ppmC)}
\end{aligned}
\qquad (5)
$$

In this set, ethylene is represented as 40% of total olefins, formaldehyde as 75% of total aldehydes, and toluene as 40% of total aromatics. The greater the source emissions distribution for hydrocarbons differs from the St. Louis case, the less appropriate these default factors will be.

## Boundary Concentration Options

Typically, values of lateral unwind boundary concentrations will be specified by the user at hour intervals based on observations from at least one ambient monitoring station upwind of the PBM domain. If it is thought that the contribution to the local pollution burden is minimal from upwind transported ozone and precursors, the user has the option of choosing a relatively clean tropospheric profile for default values of lateral boundary concentrations. These values are: CO = 0.10 ppm, NO = 0.001 ppm, $NO_2$ = 0.002 ppm, NMHC = 0.05 ppm, and $O_3$ = 0.03 ppm. These default values should not, however, be used as a substitute for knowledge about inflow boundary concentrations.

Measured boundary concentrations at the top of the model domain are generally not commonly available to the user. Without such measurements the user has the option in PBMAQE to choose an alternative method of specifying the top boundary condition for $O_3$. This method involves averaging the values of the lateral upwind boundary concentrations for $O_3$ specified during the hours of 0900-1000 and 1000-1100 L.S.T. and using the result for the top boundary concentration. It is presumed that $O_3$ in upper air layers will be

mixed to the surface after the morning low-level temperature inversion has eroded and broken; the concentration detected by upwind surface monitors at that time should be indicative of the concentration aloft. This method is applied only for $O_3$ and not for precursor species, which are not considered at the top boundary.

## Source Emissions

At the user's option, all source emissions may or may not be included in a PBM simulation. If source emissions are included, point source emissions may or may not be specified. If source emissions are specified, the preprocessor allows input in units of kg $h^{-1}$ for CO, $NO_x$, and THC and moles $h^{-1}$ for the hydrocarbon classes HC0 (NONR), HC1 (ETH and OLE), HC2 (PAR), HC3 (FORM and ALD), and HC4 (ARO and TOL). These units are converted to ppm-m $min^{-1}$ for output to the PBM. Alternatively, the user may specify emissions directly to PBMAQE in these final units and no conversions will be performed.

The source emission inputs should be resolved to hourly rates in order to generate representative hourly average concentration estimates from the PBM. Quite often, only a monthly or annual emissions rate is available for the various source configurations. In the absence of any other data that might aid in temporally distributing these emissions, the area and point source emission rates can be subdivided equally into hourly rates. For line sources however, the total daily emissions, where possible, should be distributed according to a weekday/weekend hourly traffic pattern.

Emission splits of organic compounds in the above hydrocarbon classes for most residential, commercial, and industrial processes are shown in Bucon et al. (1978). They must be specified to PBMAQE as total moles $h^{-1}$ (or ppm-m $min^{-1}$) of HC0, HC1, HC2, HC3, and HC4. The preprocessor creates the adjusted reactivity categories for the source emissions terms output to the PBM. HC0 becomes NONR, HC1 becomes ETH and OLE according to a 40%/60% split (0%/100% for point sources), HC2 becomes PAR, HC3 becomes FORM and

ALD according to a 75%/25% split (80%/20% for point sources), and HC4 becomes ARO and TOL according to a 60%/40% split (50%/50% for point sources). These splits are estimations based on work done with the St. Louis Regional Air Pollution Study emissions inventory.

Additionally, users may specify the ratio, $NO_2/NO_x$, in area source emissions and point source emissions and the ratio, $CH_4/THC$, in area source emissions and point source emissions. Default values may also be used instead. These values are 0.10, 0.10, 0.00, and 0.06, respectively.

If emissions are specified, PBMAQE expects hourly emissions fluxes in the 8 categories: CO, NOX, THC, HCO, HC1, HC2, HC3, and HC4 for the combined area and line sources and also, optionally, for the combined point sources.

## SIMULATION CONTROL DATA

### Simulation Options

An array of options is available to control various aspects of a PBM simulation. Some of the options are self-evident and need no further discussion. Options requiring less obvious choices are discussed below.

Option 5: Changing number of simulation hours.

The default period of simulation has been designed to start near sunrise and end in the late afternoon/early evening period, after the $O_3$ maximum concentration has typically been reached. At the user's option, the period of simulation may be specified as longer than the default, but not to exceed 18 hours. Appropriate input data must be specified for the additional time period. This option may also be used to shorten the simulation period. For example, if an input file exists with 13 hours of data but the user desires to end simulation after 10 hours, Option 5 is invoked and the number of hours of simulation is specified as 13 with the ending time specified as 600 minutes. Simulation start time is fixed at 0500h, LST.

Option 6: Changing numerical integration tolerance parameter.

The numerical integration routine that solves the species equations in the PBM requires a tolerance parameter within which the solution must converge. An allowable error of 1% has been specified as the default (.01). Occasionally, this value will not be sufficient for a particular simulation and the numerical solution routine will not converge, causing the simulation to consume inordinate amounts of time. To guard against such instances, a maximum time limit (e.g., 2 minutes, for a machine comparable to the UNIVAC 1100) should be specified at execution time. In a non-convergence situation, the simulation can usually be made to proceed by invoking Option 6 and raising the tolerance parameter to a value in the range of .02-.05. The larger the value, however, the greater is the amount of numerical error that will be allowed to propagate in the solution.

Option 8: Reading hourly ambient temperatures.

When hourly ambient temperatures are not specified, the temperature-dependent rate constants are calculated using a default temperature of 298°K(≈ 77°F). When actual ambient temperatures are considerably greater or less than this value, rate constants, and consequently PBM-predicted concentrations, can vary significantly from default conditions. Because ambient temperatures are usually available, it is recommended that this option always be used. For measured temperatures above 38°C (100°F), specified temperatures should indicate 38°C because the temperature-dependent rate constant expressions are not accurate above this level.

Option 9: $O_3$ boundary conditions via photostationary state.

When upwind concentrations of $O_3$ are missing or unavailable Option 9 can be used to calculate them when NO and $NO_2$ concentrations are specified at the boundary. Because this situation would probably not occur very often, the option would not commonly be used.

Option 10: Specified emissions.

With the exception of special cases or sensitivity studies, this option (explicitly specifying emissions) will always be invoked.

Domain Size

The length of a horizonal side of the fixed model domain should be chosen such that the majority of the major area and line source emissions lie within the model domain. Further guidance in choosing the proper domain size is given in the discussion of features and limitations in Section 1.

## SECTION 4

## COMPUTER ASPECTS OF THE PBM

### SYSTEM OVERVIEW

The PBM system consists of the main simulation model and two data preprocessors as depicted in Figure 3. The preprocessors, PBMMET and PBMAQE, must be executed before the PBM. Input data for all components of the system are recorded on cards or card-images. Device numbers for the card reader and printer are assumed to be 5 and 6, respectively. The user has the option of reading portions of the input card-image data from disk or tape devices. Output card-image data may also be stored on disk or tape.

The programming language used throughout the system is FORTRAN. The subroutine structures of PBMMET and the PBM are shown in Figures 4 and 5, respectively. Brief descriptions of the main programs and their subroutines are given below. Definitions of variables and array names are provided in glossaries within most main programs and subroutines.

PBMMET - Main program: reads and analyzes control information, reads remaining input parameters, processes mixing height and solar radiation data, calculates photolytic rate constants, calls CLOUD, if necessary, to determine cloud transmissivity, writes output data to printer and other data storage device.

SOLAR - Subroutine that provides, among other parameters, solar elevation and optical air mass given inputs of time and location.

SPLNA - Subroutine that sets up coefficients for cubic spline interpolation given a discrete set of (x,y) data points.

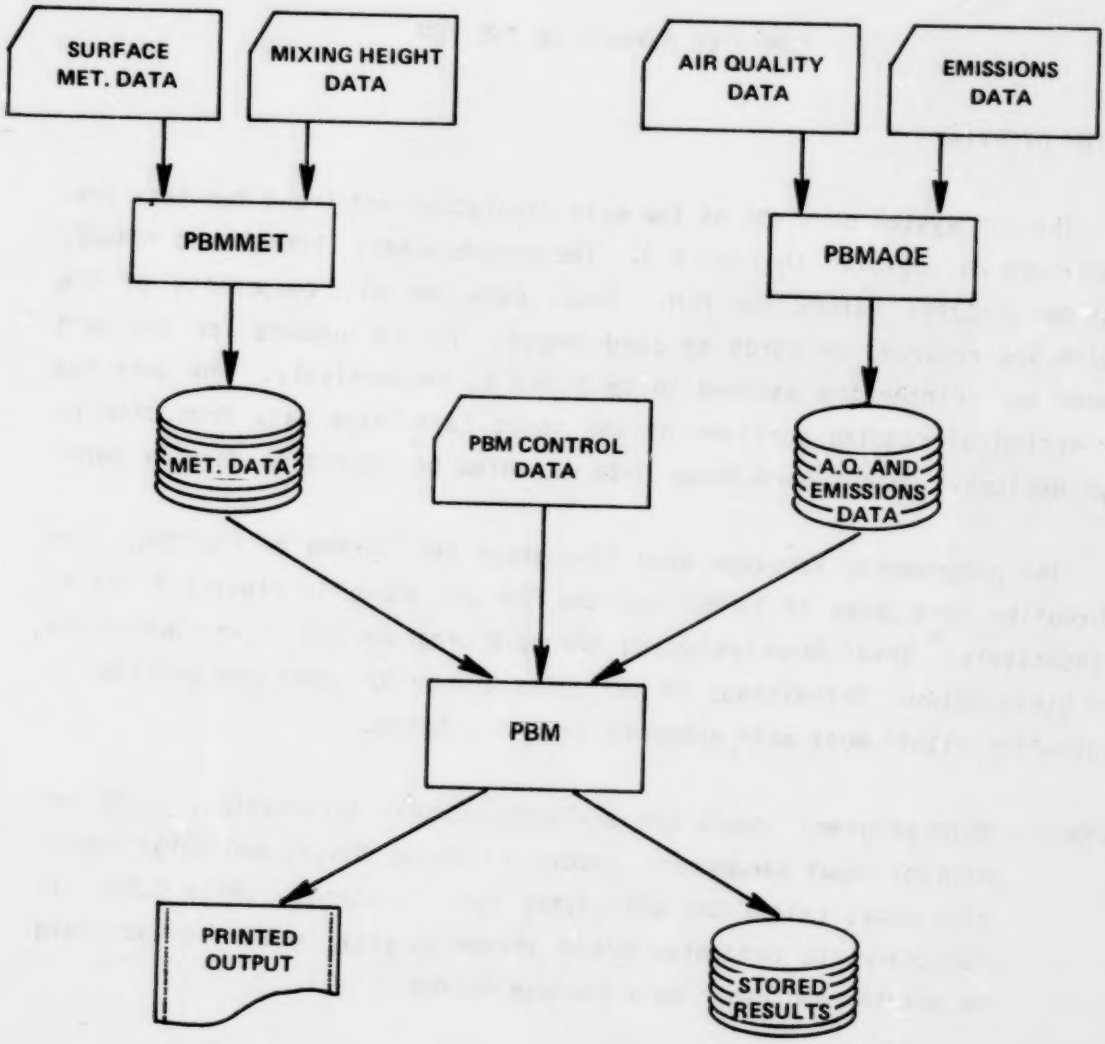



Figure 3. Schematic illustration of the PBM system.

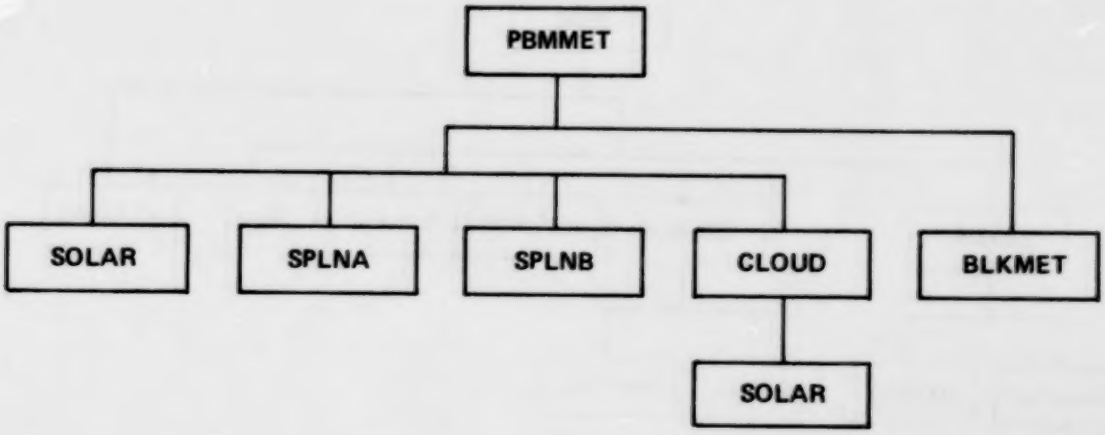



Figure 4. Subroutine structure of the PBMMET preprocessor.

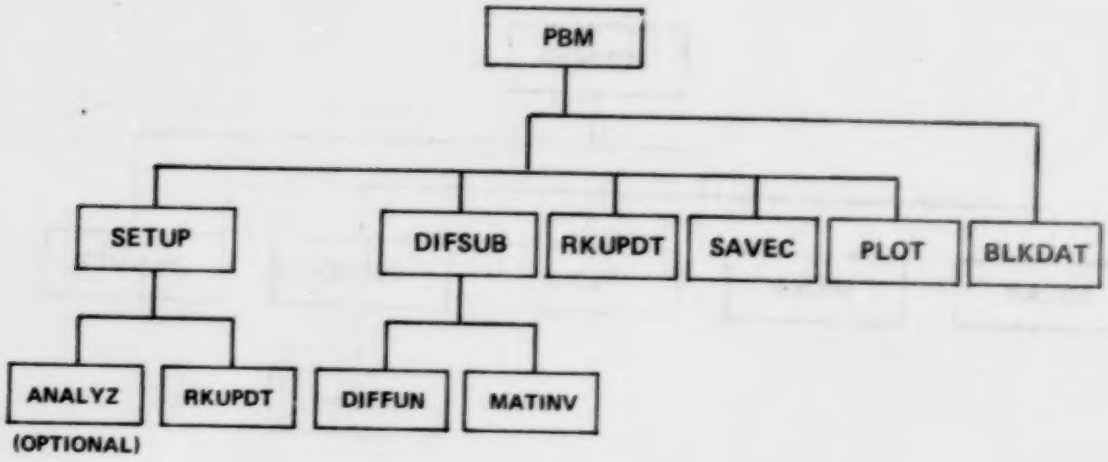



Figure 5. Subroutine structure of the PBM.

SPLNB - Subroutine that computes the interpolated value of y given any value of x within a prescribed range. It uses the cubic spline coefficients determined by SPLNA.

CLOUD - Subroutine that calculates a transmissivity factor used for attenuating photolytic rate constant values from cloud layer reports of height and sky coverage.

BLKMET - Block data that contains values of data arrays used by PBMMET, including the theoretical clear-sky values at various zenith angles of the photolytic rate constants used by the default chemical kinetic mechanism.

PBMAQE - Main program: reads and analyzes control information, processes initial concentrations, lateral and top boundary concentrations, combined area and line source emissions, combined point source emissions, and passes along species names for printer plots. (No subroutines called by PBMAQE).

PBM - Main program: Driving routine for the air quality simulation model, calls SETUP for initialization of variables, updates time and temperature-dependent rate constants and calls numerical integration routine, calls routines to do printer plots and save output data on disk/tape at end of simulation.

SETUP - Subroutine that performs initializations for the air quality simulation, reads and analyzes control options, reads all meteorological, air quality, and emissions data produced by the preprocessors, and prints out initial species concentrations.

DIFSUB - Subroutine that solves a system of differential equations using the Gear (1971) numerical method given data on initial conditions, step size, and convergence tolerance.

RKUPDT - Subroutine that calculates values of temperature-dependent reaction rate constants given the ambient temperature value.

SAVEC - Subroutine that writes out hourly values of predicted and observed (if available) concentrations of all species from the air quality simulation to disk/tape storage.

PLOT - Subroutine that produces printer plots of the time series of selected species from the air quality simulation.

BLKDAT - Block data that contains values of data variables and arrays used by PBM, including those arrays defining the structure of the default chemical kinetic mechanism.

ANALYZ - Subroutine (optionally used) that reads and analyzes a chemical kinetic mechanism other than the default mechanism for use in the PBM. (See Appendix A for further details.)

DIFFUN - Subroutine that provides the numerical solver (DIFSUB) with current rates of change of the reactive species concentrations, including the contributions from the components of chemistry, transport, vertical dilution, and source emissions.

MATINV - Subroutine that performs the matrix inversion step for DIFSUB.

## INPUT DATA PREPARATION

Data input to the PBM preprocessors and the PBM as well as output data that will be archived are recorded on cards or card-images. The user may control the storage medium for data input/output through some of the control options available in the PBM system and the control language of the particular computer system used. For purposes of illustration, the nomenclature of cards will be used in this section describing the format of the data inputs. Tables 2 through 8 describe the input format for PBMMET, the meteorological preprocessor, and Figure 6 shows its input data deck setup. Tables 9 through 25 describe the input format for PBMAQE, the air quality and emissions preprocessor, and Figure 7 shows its input data deck setup. Finally, Tables 26 through 45 describe the input format for the PBM, and Figure 8 shows its input data deck setup.

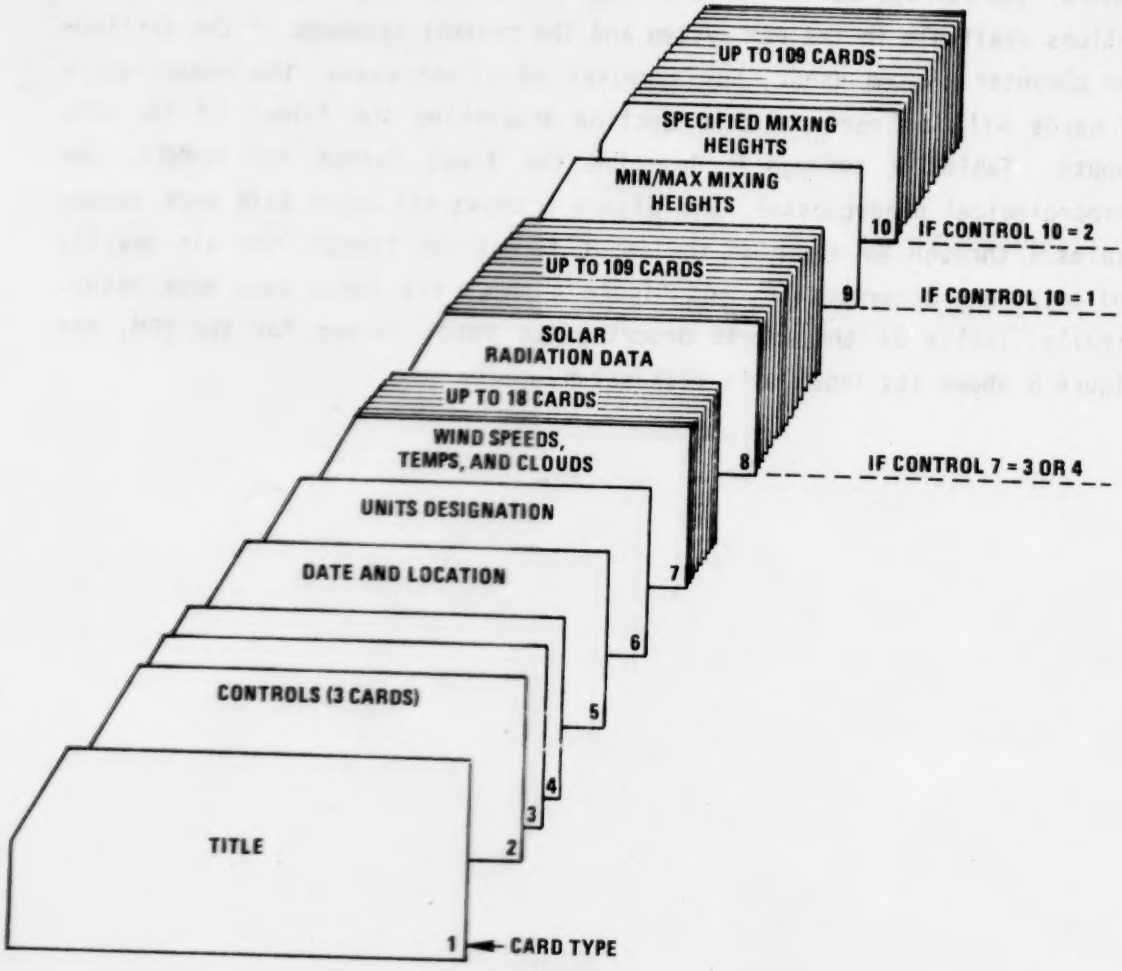



Figure 6. Input data deck setup for PBMMET.

TABLE 2. PBMMET CARD TYPE 1 - TITLE (1 card)

| Variable | Format | Description | Units |
|---|---|---|---|
| ITIT | 20A4 | 80 alphanumeric characters for title | - |

TABLE 3. PBMMET CARD TYPES 2,3, AND 4 - CONTROLS (3 cards)

| Variable | Format | Description | Units |
|---|---|---|---|
| | | CARD TYPE 2 - GENERAL CONTROLS: | |
| ICON(1) | I5 | Unit number for output device (card punch, disk, or tape) to receive and store card-image records from PBMMET. | - |
| ICON(2) | I5 | Time increment for writing outputs of mixing height and photolytic rate constants; must match the update time increment in the PBM (variable = DELTIM).<br>(Blank or 0 = DEFAULT = 10)<br>(Otherwise: 15,20,30, or 60 are allowed) | minutes |
| ICON(3) | I5 | Beginning of stop hour for processing of meteorological data, in Local Standard Time (L.S.T.)<br>(Blank or 0 = DEFAULT = 17)<br>(Maximum value allowed = 22) | hours, L.S.T. |
| ICON(4) | I5 | Not currently used. | |
| | | CARD TYPE 3 - SURFACE DATA AND SOLAR RADIATION CONTROLS: | |
| ICON(5) | I5 | Unit number for input device for reading surface meteorological observations, including wind speed, temperature, solar radiation, and cloud report data. | - |
| ICON(6) | I5 | Choice of mixed-layer average photolytic rate constants (control value = 1) or surface-based photolytic rate constants (control value = 2).<br>(Blank or 0 = DEFAULT = 1) | |

(continued)

TABLE 3 (continued)

| Variable | Format | Description | Units |
|---|---|---|---|
| ICON(7) | I5 | Photolytic rate constants are computed as follows:<br>1=Full value; clear-sky conditions<br>2=Attenuated; based on hourly cloud layer reports<br>3=Attenuated; based on measured total solar radiation every 'N' minutes (N=10,15,20,30, or 60)<br>4=Attenuated; based on measured ultraviolet radiation (wavelengths <3850A) every 'N' minutes (N=10,15,20,30, or 60).<br>(Blank or 0 = DEFAULT = 1) | |
| ICON(8) | I5 | 'N' value described in ICON(7). Radiation values will be read with this time increment from unit number specified in ICON(5).<br>(Specify value only if ICON(7) = 3 or 4) | minutes |
| | | CARD TYPE 4 - MIXING HEIGHT CONTROLS: | |
| ICON(9) | I5 | Unit number for input device for reading mixing height data. | |
| ICON(10) | I5 | Mixing heights are calculated using the following:<br>1=Daily minimum and maximum, with 'characteristic curve' method.<br>2=Input values, every 'N' minutes (N=10,15,20,30 or 60)<br>(Blank or 0=DEFAULT=1) | |
| ICON(11) | I5 | 'N' value described in ICON(10). Mixing height values will be read with this increment from unit number specified in ICON(9).<br>(Specify value only if ICON(10)=2) | minutes |

TABLE 4. PBMMET CARD TYPES 5 AND 6 - LOCATION/UNITS (2 cards)

| Variable | Format | Description | Units |
|---|---|---|---|
| | | CARD TYPE 5 - DATE AND LOCATION: | |
| IMO | I5 | Numerical designation of month (e.g., 07) | - |
| IDA | I5 | Numerical designation of day (e.g., 13) | - |
| IYR | I5 | Year (e.g., 1976) | - |
| JDA | I5,10X | Julian day number (e.g., 195) | - |
| LAT | F10.0 | Latitude of model domain (negative for southern hemisphere) | degrees |
| LONG | F10.0 | Longitude of model domain (negative for eastern hemisphere) | degrees |
| TZ | F10.0 | Number of time zones away from Greenwich Mean Time (GMT), (e.g., E.S.T. = 5.0, C.S.T. = 6.0, M.S.T. = 7.0, P.S.T. = 8.0) | - |
| | | CARD TYPE 6 - UNITS DESIGNATION: | |
| IUNW | I5 | Input wind speed data units code:<br>1=m $s^{-1}$<br>2=knots<br>3=mi $h^{-1}$ | - |
| IUNT | I5 | Input temperature data units code:<br>1=degrees-Centigrade<br>2=degrees-Fahrenheit | - |

TABLE 5. PBMMET CARD TYPE 7 - SURFACE METEOROLOGICAL DATA (up to 18 cards)

| Variable | Format | Description | Units |
|---|---|---|---|
| IHR | I5 | Beginning of hour during which surface meteorological data apply (e.g., 05) | hour, L.S.T. |
| WS | F10.0 | Wind speed during the hour | m $s^{-1}$, knots, or mi $h^{-1}$ |
| TEMPS | F10.0, 10X | Ambient temperature during the hour | deg-C or deg-F |
| The following variables are specified only if ICON(7)=2 on CARD TYPE 3: | | | |
| ICA(1) | A1,4X | Sky coverage, in tenths, of clouds in 1st reported layer during the hour. (Blank=no report or clear; 1 through 9; or '-'=10 are allowed) | - |
| ICH(1) | A3,2X | Height of 1st cloud layer (Blank=no report) | hundreds of ft, agl |
| ICA(2) | A1,4X | Cumulative sky coverage, in tenths, of clouds in 1st and 2nd reported layers, if given, during the hour. | - |
| ICH(2) | A3,2X | Height of 2nd cloud layer | hundreds of ft, agl |
| ICA(3) | A1,4X | Cumulative sky coverage, in tenths, of clouds in 1st , 2nd, and 3rd reported layers, if given, during the hour. | - |
| ICH(3) | A3 | Height of 3rd cloud layer | hundreds of ft, agl |

TABLE 6. PBMMET CARD TYPE 8 - SOLAR RADIATION DATA (up to 109 cards) (used with ICON(7) = 3 or 4)

| Variable | Format | Description | Units |
|---|---|---|---|
| IT | I5 | Time at which radiation value applies (e.g., 1040) | hours, L.S.T. |
| RAD | F10.0 | Measured value of solar radiation data:<br><br>Total solar radiation if ICON(7)=3<br>Ultraviolet radiation if ICON(7)=4<br>(Radiation values must be specified for the entire simulation period. Values of 0 should be entered for other than daytime conditions. Last specified value must be -1.0). | langleys $min^{-1}$ |

TABLE 7. PBMMET CARD TYPE 9 - MIN/MAX MIXING HEIGHTS (1 card) (used with ICON(10=1)

| Variable | Format | Description | Units |
|---|---|---|---|
| HMIN0 | 5X, F10.0 | Height above ground of the morning minimum depth of the mixed layer. (For values < 100 m, use 100 m). | meters |
| HMAX | F10.0 | Height above ground of the afternoon maximum depth of the mixed layer. (For values > 2000 m, use 2000 m). | meters |
| HMIN1 | F10.0 | Height above ground of the next morning minimum depth of the mixed layer. (For values < 100 m, use 100 m). | meters |

TABLE 8. PBMMET CARD TYPE 10 - SPECIFIED MIXING HEIGHTS (up to 109 cards) (used with ICON(10)=2)

| Variable | Format | Description | Units |
|---|---|---|---|
| IT | I5 | Time at which mixing height value applies (e.g., 1040) | hours, L.S.T. |
| HEIGHT | F10.0 | Depth of the mixed layer. (100<HEIGHT<2000) (Last specified value must be -1.0) | meters |

TABLE 9. PBMAQE CARD TYPE 1 - TITLE (1 card)

| Variable | Format | Description | Units |
|---|---|---|---|
| ITIT | 20A4 | 80 alphanumeric characters for title | - |

TABLE 10. PBMAQE CARD TYPE 2 - SIMULATION CONTROLS (1 card)

| Variable | Format | Description | Units |
|---|---|---|---|
| WIDTH | F10.0 | Size of horizontal edge of PBM domain | km |
| TEMP | F10.0 | Average ambient temperature during simulation period | deg-C |
| NUMHR | I5 | Number of hours of data to be processed by PBMAQE and simulated by the PBM (Blank or 0=DEFAULT=13) | - |

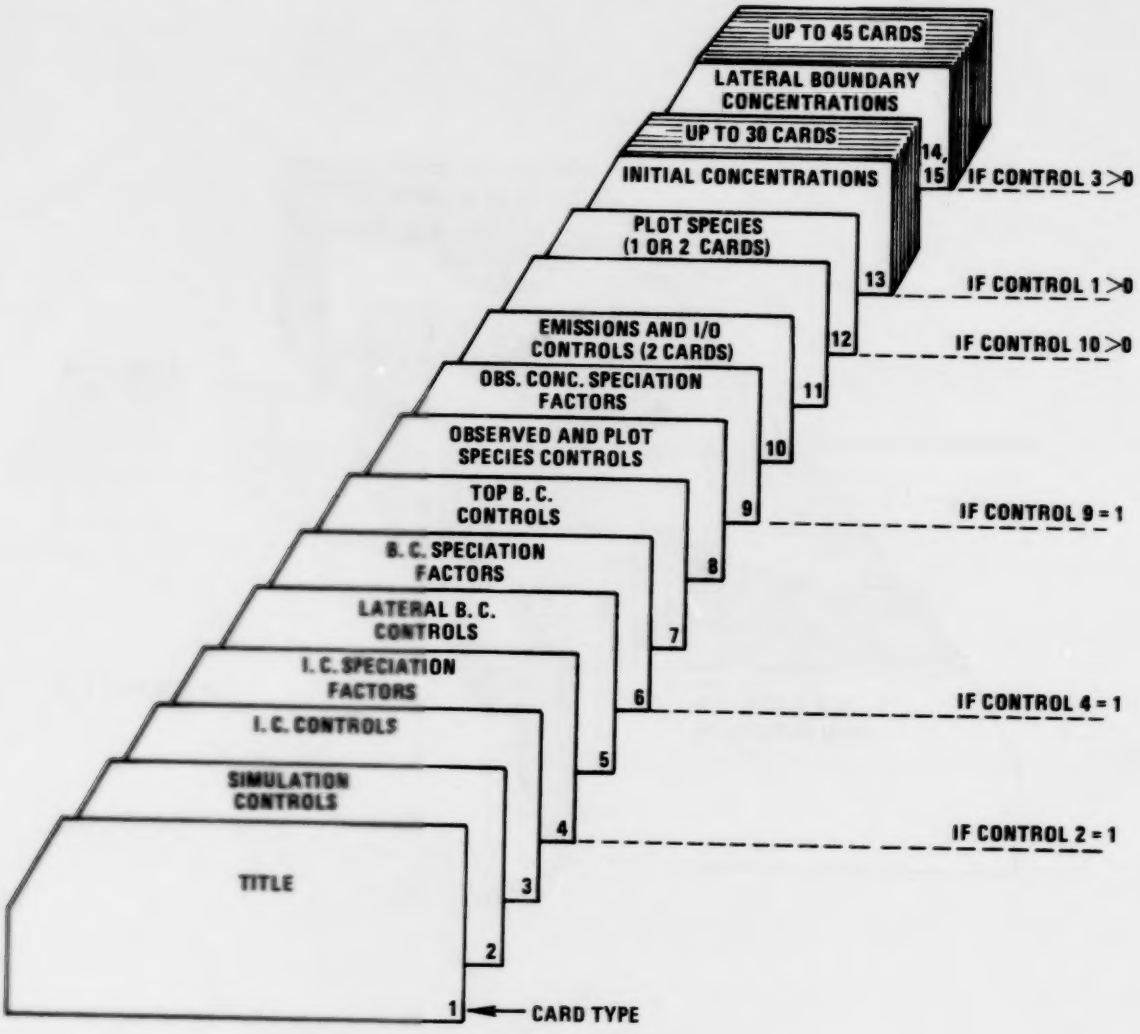



Figure 7. Input data deck setup for PBMAQE.

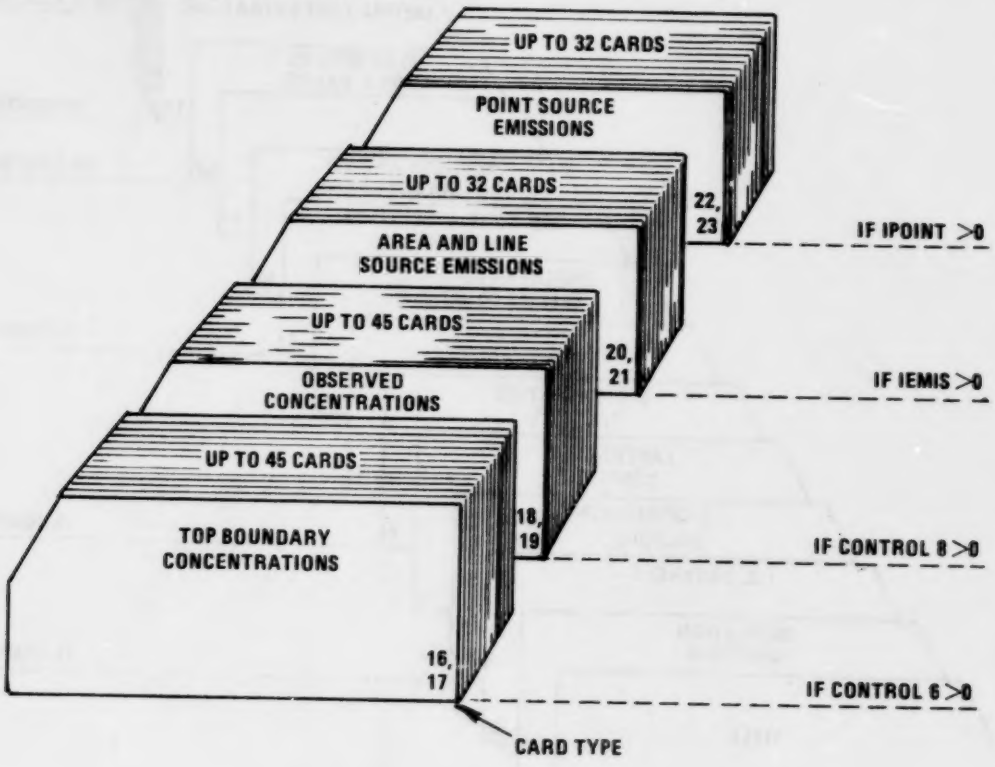



Figure 7. (continued)

TABLE 11. PBMAQE CARD TYPE 3 - I.C. CONTROLS (1 card)

| Variable | Format | Description | Units |
|---|---|---|---|
| ICON(1) | I5 | Number of initial species concentrations to be specified for 0500h, L.S.T. (Do not count hydrocarbon reactivity classes in the sum.) | - |
| ICON(2) | I5 | Input values of hydrocarbon speciation factors for initial NMHC? (Blank or 0=DEFAULT=no; St. Louis default values will be used. 1=yes.) | |

TABLE 12. PBMAQE CARD TYPE 4 - I.C. SPECIATION FACTORS (1 card) (used with ICON(2) = 1)

| Variable | Format | Description | Units |
|---|---|---|---|
| SFIC | 8F10.0 | Hydrocarbon speciation factors to split initial NMHC concentration into 8 reactivity classes | - |

TABLE 13. PBMAQE CARD TYPE 5 - LATERAL B.C. CONTROLS (1 card)

| Variable | Format | Description | Units |
|---|---|---|---|
| ICON(3) | I5 | Number of lateral boundary condition species to be specified (maximum=15) | - |
| ICON(4) | I5 | Input values of hydrocarbon speciation factors for NMHC boundary concentrations (lateral and top)? (Blank or 0=DEFAULT=no; St. Louis default values will be used. 1=yes.) | - |
| ICON(5) | I5 | Use 'clean troposphere' values for lateral boundary concentrations? (Blank or 0=DEFAULT=no; user will input hourly values of boundary concentrations. 1=yes; values will be set implicitly, ICON(3) must be set to 0.) | - |

TABLE 14. PBMAQE CARD TYPE 6 - B.C. SPECIATION FACTORS (1 card) (used with ICON(4)=1)

| Variable | Format | Description | Units |
|---|---|---|---|
| SFBC | 8F10.0 | Hydrocarbon speciation factors to split NMHC boundary concentrations (lateral and top) into 8 reactivity classes | - |

TABLE 15. PBMAQE CARD TYPE 7 - TOP B.C. CONTROLS (1 card)

| Variable | Format | Description | Units |
|---|---|---|---|
| ICON(6) | I5 | Number of top boundary condition species to be specified. (maximum=15) | - |
| ICON(7) | I5 | Top $O_3$ boundary concentration to be determined implicitly from lateral $O_3$ boundary concentrations? (Blank or 0=DEFAULT=no, 1=yes; do not count $O_3$ in total value of ICON(6) ) | |

TABLE 16. PBMAQE CARD TYPE 8 - OBSERVED AND PLOT SPECIES CONTROLS (1 card)

| Variable | Format | Description | Units |
|---|---|---|---|
| ICON(8) | I5 | Number of observed species to be specified. (maximum=15) | - |
| ICON(9) | I5 | Input values of hydrocarbon speciation factors for NMHC observed concentrations? (Blank or 0=DEFAULT=no; St. Louis default values will be used. 1=yes.) | - |
| ICON(10) | I5 | Number of species to be plotted on printer during PBM simulation. (maximum=30) | - |

TABLE 17. PBMAQE CARD TYPE 9 - OBS. CONC. SPECIATION FACTORS (1 card) (used with ICON(9)=1)

| Variable | Format | Description | Units |
|---|---|---|---|
| SFOB | 8F10.0 | Hydrocarbon speciation factors to split NMHC observed concentrations into 8 reactivity classes. | - |

TABLE 18. PBMAQE CARD TYPES 10 AND 11 - EMISSIONS AND I/O CONTROLS (2 cards)

| Variable | Format | Description | Units |
|---|---|---|---|
| | | CARD TYPE 10 - EMISSIONS CONTROLS: | |
| IEMIS | I5 | Input emissions code:<br>Blank or 0 = No emissions specified.<br>1=CO,$NO_x$,THC emissions specified in kg $h^{-1}$;<br>HCO,HC1,...,HC4 emissions specified in moles $h^{-1}$.<br>2=CO,$NO_x$,THC,HCO,HC1,...,HC4 emissions specified in ppm-m $min^{-1}$. | - |
| IPOINT | I5 | Point source flag:<br>Blank or 0=no point emissions specified<br>1=point source emissions specified in same units indicated by IEMIS | - |
| RATIO(1) | 2X, F8.0 | Ratio of $NO_2/NO_x$ in combined area and line source emissions | - |
| RATIO(2) | 2X, F8.0 | Ratio of $NO_2/NO_x$ in point source emissions | - |
| RATIO(3) | 2X, F8.0 | Ratio of $CH_4$/THC in combined area and line source emissions | - |
| RATIO(4) | 2X, F8.0 | Ratio of $CH_4$/THC in point source emissions (If RATIO(1) and RATIO(3) are both blank, defaults of 0.10 and 0.00, respectively will be used. If RATIO(2) and RATIO(4) are both blank, defaults of 0.10 and 0.06, respectively will be used. Otherwise, specified values will be used.) | - |
| | | CARD TYPE 11 - I/O CONTROLS: | |
| NAQ | I5 | Input unit number for air quality values. | |
| NEM | I5 | Input unit number for emissions values | - |
| NOUTD | I5 | Output unit number for card, disk, or tape storage of card-image data for the PBM | - |

TABLE 19. PBMAQE CARD TYPE 12 - PLOT SPECIES (1 or 2 cards)
(used with ICON(10)>0)

| Variable | Format | Description | Units |
|---|---|---|---|
| NPLOT | 20A4 | Alphanumeric names of species to be plotted on printer by the PBM. | - |

TABLE 20. PBMAQE CARD TYPE 13 - INITIAL CONCENTRATIONS (up to 30 cards)
(used with ICON(1)>0)

| Variable | Format | Description | Units |
|---|---|---|---|
| ISPEC | A4 | Alphanumeric name of i.c. species | - |
| CI | 6X, F10.0 | Species concentrations at 0500h, L.S.T. | ppm |

TABLE 21. PBMAQE CARD TYPES 14 AND 15 - LATERAL BOUNDARY CONCENTRATIONS
(up to 45 cards)
(used with ICON(3)>0)

| Variable | Format | Description | Units |
|---|---|---|---|
| | | CARD TYPE 14 - SPECIES NAME: (1 card per species) | |
| ISPEC | A4 | Alphanumeric name of lateral b.c. species | - |
| | | CARD TYPE 15 - B.C. CONCENTRATIONS: (1 or 2 cards per species) | |
| CLAT | 10F8.0 | Hour-average lateral boundary concentrations of ISPEC for each hour of PBM simulation | ppm |

TABLE 22. PBMAQE CARD TYPES 16 AND 17 - TOP BOUNDARY CONCENTRATIONS (up to 45 cards) (used with ICON(6)>0)

| Variable | Format | Description | Units |
|---|---|---|---|
| | CARD TYPE 16 - SPECIES NAME: (1 card per species) | | |
| ISPEC | A4 | Alphanumeric name of top b.c. species | - |
| | CARD TYPE 17 - B.C. CONCENTRATIONS: (1 or 2 cards per species) | | |
| C | 10F8.0 | Hour-average top boundary concentrations of ISPEC for each hour of PBM simulation | ppm |

TABLE 23. PBMAQE CARD TYPES 18 AND 19 - OBSERVED CONCENTRATIONS (up to 45 cards) (used with ICON(8)>0)

| Variable | Format | Description | Units |
|---|---|---|---|
| | CARD TYPE 18 - SPECIES NAME: (1 card per species) | | |
| ISPEC | A4 | Alphanumeric name of observed species | - |
| | CARD TYPE 19 - OBSERVED CONCENTRATIONS: (1 or 2 cards per species) | | |
| C | 10F8.0 | Hour-average observed concentrations of ISPEC for each hour of PBM simulation. (-1.0 indicates missing data). | ppm |

TABLE 24. PBMAQE CARD TYPES 20 AND 21 - AREA AND LINE SOURCE EMISSIONS (up to 32 cards) (used with IEMIS>0)

| Variable | Format | Description | Units |
|---|---|---|---|
| | CARD TYPE 20 - SPECIES NAME: (1 card per species) | | |
| ISPEC | A4 | Alphanumeric name of emissions species | - |
| | CARD TYPE 21 - EMISSIONS: (up to 3 cards per species) | | |
| C | 8F10.0 | Hourly emissions flux of ISPEC for combined area and line source emissions into PBM domain for each hour of simulation. Species must conform exactly to the 8 specified in Section 3. | Kg $h^{-1}$ and moles $h^{-1}$ (if IEMIS=1); ppm-m $min^{-1}$ (if IEMIS=2) |

TABLE 25. PBMAQE CARD TYPES 22 AND 23 - POINT SOURCE EMISSIONS (up to 32 cards) (used with IPOINT>0)

| Variable | Format | Description | Units |
|---|---|---|---|
| | CARD TYPE 22 - SPECIES NAME: (1 card per species) | | |
| ISPEC | A4 | Alphanumeric name of emissions species | - |
| | CARD TYPE 23 - EMISSIONS: (up to 3 cards per species) | | |
| CLAT | 8F10.0 | Hourly emissions flux of ISPEC for point source emissions into PBM domain for each hour of simulation. Species must conform exactly to the 8 specified in Section 3. | Kg $h^{-1}$ and moles $h^{-1}$ (if IEMIS=1); ppm-m $min^{-1}$ (if IEMIS=2) |

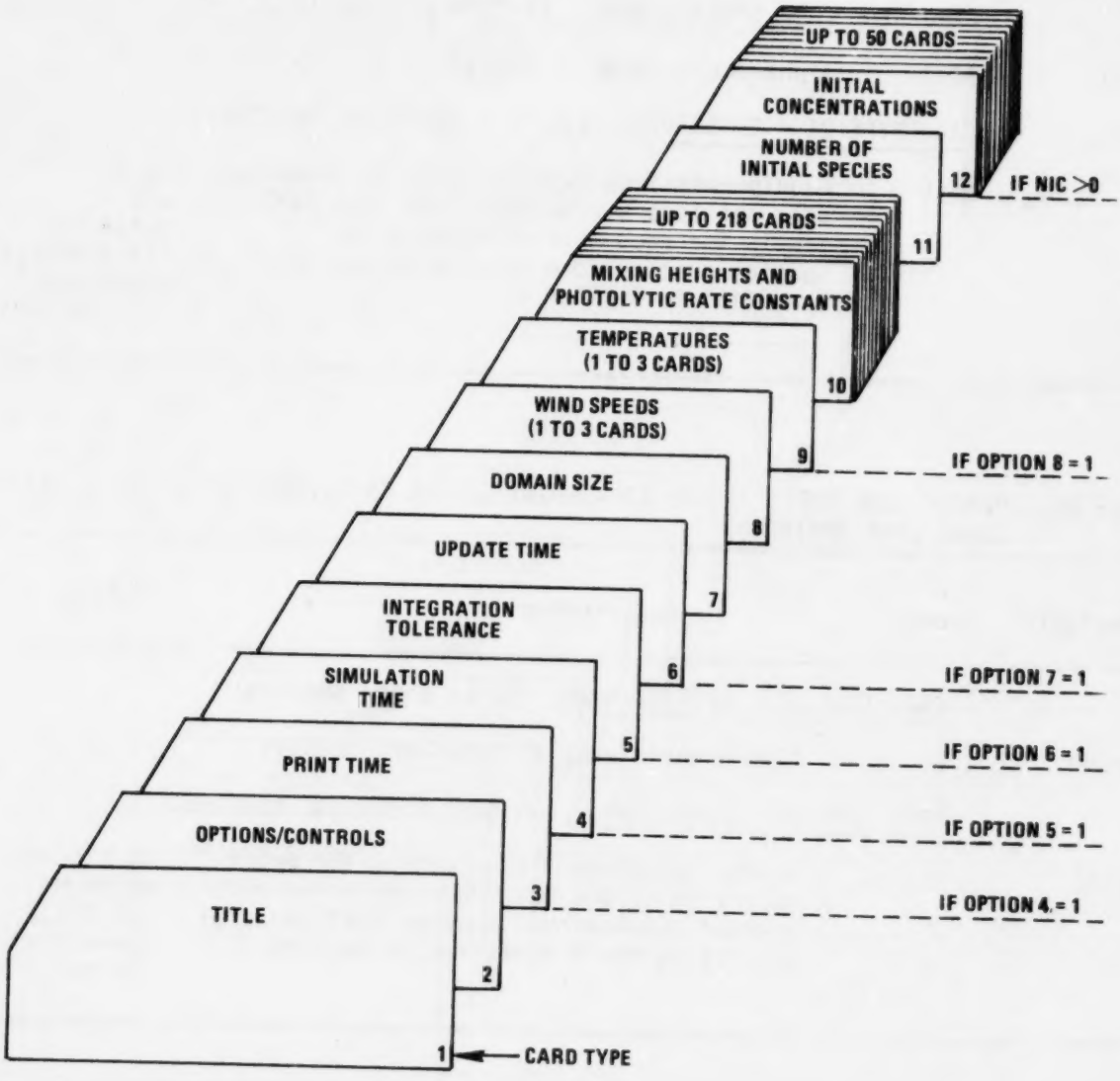



Figure 8. Input data deck setup for the PBM.

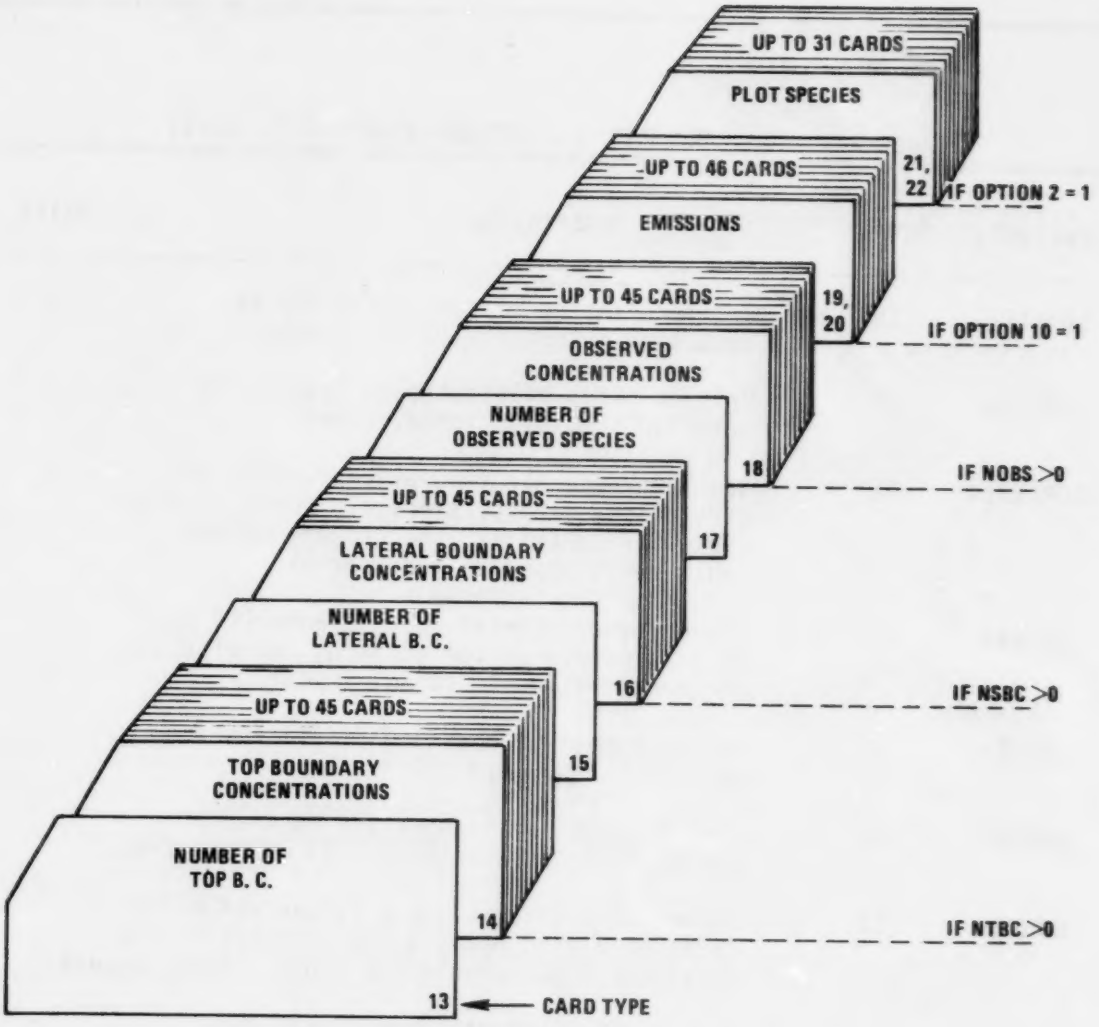



Figure 8. (continued)

TABLE 26. PBM CARD TYPE 1 - TITLE (1 card)

| Variable | Format | Description | Units |
|---|---|---|---|
| NTIT | 20A4 | 80 alphanumeric characters for title | - |

TABLE 27. PBM CARD TYPE 2 - OPTIONS/CONTROLS (1 card)

| Variable | Format | Description | Units |
|---|---|---|---|
| IOPT(1) | I5 | Printed listing of concentrations at each time interval? (0=no, 1=yes) | - |
| IOPT(2) | I5 | Printer plots of simulation results for selected species? (0=no, 1=yes) | - |
| IOPT(3) | I5 | Save hour-average simulation results on card, disk, or tape storage? (0=no, 1=yes) (Note: If IOPT(3)=1, the storage device must be assigned unit number 8) | - |
| IOPT(4) | I5 | Change time interval from default (10 min) to a larger value for printing and plotting of concentrations? (0=no, 1=yes) | - |
| IOPT(5) | I5 | Change number of hours of simulation from default (13 hours)? (0=no, 1=yes) | - |
| IOPT(6) | I5 | Change numerical integration tolerance parameter from default (0.01)? (0=no, 1=yes) | - |
| IOPT(7) | I5 | Change time interval to a larger value for updating mixing heights and photolytic rate constants from default (10 min)? (0=no, 1=yes) | |
| IOPT(8) | I5 | Read hourly ambient temperatures for temperature-dependent rate constant calculations? (0=no, 1=yes) | - |
| IOPT(9) | I5 | Steady-state lateral boundary concentration for $O_3$? (0=no, 1=yes) | - |
| IOPT(10) | I5 | Read emissions rates for simulation? (0=no, 1=yes) | - |

TABLE 28. PBM CARD TYPE 3 - PRINT TIME (1 card)
(used with IOPT (4)=1)

| Variable | Format | Description | Units |
|---|---|---|---|
| TINCR | F10.0 | Time interval for printing and plotting of predicted concentrations. Allowable values are 10.,15.,20.,30., and 60. (Default=10.) | minutes |

TABLE 29. PBM CARD TYPE 4 - SIMULATION TIME (1 card)
(used with IOPT(5)=1)

| Variable | Format | Description | Units |
|---|---|---|---|
| NUMHR | I5 | Number of hours of simulation data to be read in. (Default=13)(Must agree with NUMHR of PBMAQE - see Table 10) | - |
| TEND | F10.0 | Stop time of simulation, in minutes after 0500h, L.S.T. (TEND is usually set to a value of 60.*NUMHR, but it may be set less than this value.) | minutes |

TABLE 30. PBM CARD TYPE 5 - INTEGRATION TOLERANCE (1 card)
(used with (IOPT(6)=1)

| Variable | Format | Description | Units |
|---|---|---|---|
| EPSF | F10.0 | Numerical integration tolerance parameter. (Default=0.01) | - |

TABLE 31. PBM CARD TYPE 6 - UPDATE TIME (1 card)
(used with IOPT(7)=1)

| Variable | Format | Description | Units |
|---|---|---|---|
| DELTIM | F10.0 | Time interval for updating mixing heights and photolytic rate constants. Allowable values are 10.,20.,30., and 60. (Default=10.)(Must agree with ICON(2) of PBMMET - see Table 3) | minutes |

TABLE 32. PBM CARD TYPE 7 - DOMAIN SIZE (1 card)

| Variable | Format | Description | Units |
|---|---|---|---|
| WIDTH | F10.0 | Size of horizontal edge of PBM domain. | km |

Card-image input to the PBM described in Tables 26-32 must be prepared by the user for an execution of the PBM. Card-image input described in Tables 33-45 is prepared for the PBM by the preprocessors PBMMET and PBMAQE.

TABLE 33. PBM CARD TYPE 8 - WIND SPEEDS (up to 3 cards)

| Variable | Format | Description | Units |
|---|---|---|---|
| WS | 8F10.0 | Average wind speed for each hour of simulation. | m s-1 |

TABLE 34. PBM CARD TYPE 9 - TEMPERATURES (up to 3 cards) (used with IOPT(8)=1)

| Variable | Format | Description | Units |
|---|---|---|---|
| TEMPS | 8F10.0 | Average ambient temperature for each hour of simulation. | deg-C |

TABLE 35. PBM CARD TYPE 10 - MIXING HEIGHTS AND PHOTOLYTIC RATE CONSTANTS (up to 218 cards)

| Variable | Format | Description | Units |
|---|---|---|---|
| ITIME | I5 | Time at which data apply. (Time interval between data inputs must agree with DELTIM -- see Table 31.) | hours, L.S.T. |
| HTMIX | 5X,F10.0 | Depth of the mixed layer at current time (100<HTMIX<2000) (Last specified value must be =-1.0). | meters |
| PRC | 6E10.0,/, 20X,6E10.0 | Photolytic rate constants at current time for chemical species that participate in photolysis reactions. | minute$^{-1}$ |

TABLE 36. PBM CARD TYPE 11 - NUMBER OF INITIAL SPECIES ( 1 card)

| Variable | Format | Description | Units |
|---|---|---|---|
| NIC | I5 | Number of initial species concentrations to be specified for 0500h, L.S.T. (maximum=50) | - |

TABLE 37. PBM CARD TYPE 12 - INITIAL CONCENTRATIONS (up to 50 cards) (used with NIC>0)

| Variable | Format | Description | Units |
|---|---|---|---|
| ISPEC | A4 | Alphanumeric name of i.c. species | - |
| CI | 6X,E10.0 | Species concentration at 0500h, L.S.T. | ppm |

TABLE 38. PBM CARD TYPE 13 - NUMBER OF TOP B.C. (1 card)

| Variable | Format | Description | Units |
|---|---|---|---|
| NTBC | I5 | Number of top boundary condition species to be specified. (maximum=15) | - |

TABLE 39. PBM CARD TYPE 14 - TOP BOUNDARY CONCENTRATIONS (up to 45 cards) (used with NTBC>0)

| Variable | Format | Description | Units |
|---|---|---|---|
| ISPEC | A4 | Alphanumeric name of top b.c. species | - |
| TPCONC | 6X,7E10.0, /,(10X,7E10.0) | Hour-average top boundary concentrations of ISPEC for each hour of PBM simulation. | ppm |

TABLE 40. PBM CARD TYPE 15 - NUMBER OF LATERAL B.C. (1 card)

| Variable | Format | Description | Units |
|---|---|---|---|
| NSBC | I5 | Number of lateral boundary condition species to be specified. (maximum=15) | - |

TABLE 41. PBM CARD TYPE 16 - LATERAL BOUNDARY CONCENTRATIONS (up to 45 cards) (used with NSBC>0)

| Variable | Format | Description | Units |
|---|---|---|---|
| ISPEC | A4 | Alphanumeric name of lateral b.c. species | - |
| SDCONC | 6X,7E10.0, /,(10X, 7E10.0) | Hour-average lateral boundary concentrations of ISPEC for each hour of PBM simulation | ppm |

TABLE 42. PBM CARD TYPE 17 - NUMBER OF OBSERVED SPECIES (1 card)

| Variable | Format | Description | Units |
|---|---|---|---|
| NOBS | I5 | Number of observed species to be specified. (maximum=15) | - |

TABLE 43. PBM CARD TYPE 18 - OBSERVED CONCENTRATIONS (up to 45 cards) (used with NOBS>0)

| Variable | Format | Description | Units |
|---|---|---|---|
| ISPEC | A4 | Alphanumeric name of observed species | - |
| OBS | 6X,7E10.0, /,(10X, 7E10.0) | Hour-average observed concentrations of ISPEC for each hour of PBM simulation. (-1.0 indicates missing data) | ppm |

TABLE 44. PBM CARD TYPES 19 AND 20 - EMISSIONS (up to 46 cards) (used with IOPT(10)=1)

| Variable | Format | Description | Units |
|---|---|---|---|
| | | CARD TYPE 19 - NUMBER OF EMISSIONS SPECIES: (1 card) | |
| NEMIS | I5 | Number of emissions species to be specified. (maximum=15; NEMIS must equal 12 when using the default chemical mechanism in the PBM) | - |
| | | CARD TYPE 20 - EMISSION FLUXES: (up to 3 cards per species) | |
| ISPEC | A4 | Alphanumeric name of emissions species | - |
| EMIS | 6X,7E10.0, /,(10X, 7E10.0) | Hourly emissions flux of ISPEC from all sources into PBM domain for each hour of simulation. | ppm-m $min^{-1}$ |

TABLE 45. PBM CARD TYPES 21 AND 22 - PLOT SPECIES (up to 31 cards) (used with IOPT(2)=1)

| Variable | Format | Description | Units |
|---|---|---|---|
| | | CARD TYPE 21 - NUMBER OF PLOT SPECIES: ( 1 card) | |
| NPLOT | I5 | Number of species to be plotted on printer (maximum=30) | - |
| | | CARD TYPE 22 - NAMES OF PLOT SPECIES: (up to 30 cards) | |
| ISPEC | A4 | Alphanumeric name of species to be plotted on printer. | - |

## REQUIRED RESOURCES FOR THE PBM SYSTEM

Running the PBM and its preprocessors on a particular computer system requires some knowledge of the system resources needed for the procedure. The figures provided here are intended only as a rough guide since each computer system and model application will be different. The PBM system is installed on the EPA's UNIVAC 1110 computer; the following figures are taken from a model application to St. Louis, MO using that machine.

PBMMET (Meteorological Preprocessor)

25K words of memory required
8.5 s of computer time (88%-CPU, 12% - IO)
6-11 pages of printed output

PBMAQE (Air Quality and Emissions Preprocessor)

10K words of memory required
7.5 s of computer time (90%-CPU, 10%-IO)
9 pages of printed output

PBM (Photochemical Box Model)

45K words of memory required
30 - 90 s of computer time (90%-CPU, 10%-IO)
60 - 70 pages of printed output (all information printed)
10-30 pages of printed output (plots and concentrations summary only)

The actual amount of computer time required by the PBM and its preprocessors will, of course, depend on the length of the simulation. The figures cited above are for the standard 13h simulation, starting at 0500h, L.S.T. A failure of the numerical solution to converge will cause the PBM to consume a large amount of computer time without advancing the simulation.

To guard against this occurrence, a maximum time limit (90-120 s) should be specified for every execution of the PBM. If the solution fails to converge, the tolerance may be relaxed from the default (0.01) to a value between 0.01 and 0.05 until a convergence is reached. The appropriate parameter is EPSF in the simulation controls (see Table 30). The larger the value that EPSF is allowed to take the greater is the potential for numerical errors in the solution.

# SECTION 5

# EXAMPLE PROBLEM

## DESCRIPTION

An example problem is shown here as an aid to the user in applying the PBM system. Input data and program output are given for the two preprocessors and the simulation model. The example illustrates the application of the PBM to the city of St. Louis, MO using the extensive RAPS data base (Schere and Shreffler, 1982). The model domain has 20-km horizontal sides and is centered on the downtown area. The scenario modeled occurred on Oct. 1, 1976, a day with light winds, subsidence aloft, and air stagnation near the surface. Locally generated products of photochemical activity were observed at considerably high concentrations.

Twelve surface-based meteorological and air quality monitors and one upper-air sounding location were available within the PBM domain for determining input data for the model and preprocessors. Data were averaged over all 12 monitors to determine PBM domain-average values. Nine monitors surrounding the domain were available for determining boundary concentrations. The RAPS data base also included a complete source emissions inventory for St. Louis.

The number of user-specified options among the inputs to the model and preprocessors is sufficiently large so that not all possibilities may be illustrated in the following example problem. However, the options chosen here probably represent some of the more commonly chosen ones within a large user group with a variety of applications.

Input data, UNIVAC runstream, and program output are presented. In the graphs shown in the example problem, the model-predicted instantaneous concentrations are represented by the '*'s, the predicted hour-average concentrations are represented by the 'H's, and the hour-average observed values are represented by the 'O's.

## DATA INPUT AND PROGRAM OUTPUT

UNIVAC RUNSTREAM FOR EXAMPLE PROBLEM

```
      1      @RUN ...
      2      @
      3      @
      4      @ASG,A PBM.
      5      @ASG,UP METDATA.
      6      @USE 2.,METDATA.
      7      @XQT PBM.PBMMET
      8      @ADD PBM.PBMMET-INPUT
      9      @
     10      @
     11      @ASG,UP AQEDATA.
     12      @USE 3.,AQEDATA.
     13      @XQT PBM.PBMAQE
     14      @ADD PBM.PBMAQE-INPUT
     15      @
     16      @
     17      @ASG,UP SAVERESULTS.
     18      @USE 8.,SAVERESULTS.
     19      @XQT PBM.PBM
     20      PBM - DAY 76275 - 10/01/76  (EXAMPLE PROBLEM)
     21          0    1    1    0    0    0    0    1    0    1
     22            20.0
     23      @ADD METDATA.
     24      @ADD AQEDATA.
     25      @
     26      @
     27      @FIN
**
```

INPUT DATA - PBMMET EXAMPLE PROBLEM

```
 1        TEST OF PBMMET  -  76275
 2          2
 3          5    1     3   10
 4          5    1
 5         10   01 1976  275                    38.617    90.193        6.0
 6          1    1
 7        5.0     1.583        11.1
 8        6.0     1.679        11.6
 9        7.0     1.513        14.5
10        8.0      .862        17.8
11        9.0      .391        20.8
12       10.0      .386        23.5
13       11.0      .805        25.5
14       12.0      .086        26.9
15       13.0      .479        27.8
16       14.0      .709        28.5
17       15.0      .792        28.7
18       16.0      .888        28.2
19       17.0      .896        26.1
20       5.00     .0000
21       5.17     .0000
22       5.33     .0000
23       5.50     .0000
24       5.67     .0000
25       5.83     .0000
26       6.00     .0000
27       6.17     .0059
28       6.33     .0254
29       6.50     .0556
30       6.67     .0936
31       6.83     .1308
32       7.00     .1739
33       7.17     .2178
34       7.33     .2647
35       7.50     .3086
36       7.67     .3512
37       7.83     .3954
38       8.00     .4414
39       8.17     .4872
40       8.33     .5311
41       8.50     .5671
42       8.67     .6034
43       8.83     .6390
44       9.00     .6788
45       9.17     .7141
46       9.33     .7507
47       9.50     .7825
48       9.67     .8146
49       9.83     .8374
50      10.00     .8659
51      10.17     .8933
52      10.33     .9152
53      10.50     .9388
54      10.67     .9504
55      10.83     .9689
56      11.00     .9783
```

```
INPUT DATA - PBMMET EXAMPLE PROBLEM

    57      11.17      .9925
    58      11.33     1.0090
    59      11.50     1.0094
    60      11.67     1.0197
    61      11.83     1.0085
    62      12.00     1.0088
    63      12.17      .9914
    64      12.33      .9824
    65      12.50      .9796
    66      12.67      .9813
    67      12.83      .9764
    68      13.00      .9582
    69      13.17      .9374
    70      13.33      .9101
    71      13.50      .8843
    72      13.67      .8555
    73      13.83      .8301
    74      14.00      .7981
    75      14.17      .7607
    76      14.33      .7289
    77      14.50      .6871
    78      14.67      .6533
    79      14.83      .6162
    80      15.00      .5854
    81      15.17      .5471
    82      15.33      .5074
    83      15.50      .4684
    84      15.67      .4232
    85      15.83      .3774
    86      16.00      .3344
    87      16.17      .2957
    88      16.33      .2533
    89      16.50      .2163
    90      16.67      .1802
    91      16.83      .1406
    92      17.00      .1015
    93      17.17      .0642
    94      17.33      .0319
    95      17.50      .0083
    96      17.67      .0000
    97      17.83      .0000
    98      18.00      .0000
    99                 -1.0
   100                 100.0      532.0      100.0
**
```

```
PBMMET -- METEOROLOGICAL PREPROCESSOR FOR THE PHOTOCHEMICAL BOX MODEL
**********************************************************************
TEST OF PBMMET  -  76275

SUMMARY OF CONTROLS:

  TIME INC. FOR OUTPUT OF MIX. HT. AND PHOTOLYTIC RATE CONST. =  10 MIN.

  OUTPUT DATA STORED ON UNIT NUMBER  2

  HOURLY SURFACE METEOROLOGICAL DATA READ FROM UNIT NUMBER  5

  MIXING HEIGHT DATA INPUT ON UNIT NUMBER  5

  MIXING HEIGHTS CALCULATED FROM CHARACTERISTIC CURVE METHOD

  PHOTOLYTIC RATE CONSTANTS (PRC'S) ARE AVERAGED THROUGH THE MIXED LAYER DEPTH

  PRC'S ARE ATTENUATED BASED ON MEASURED TOTAL SOLAR RADIATION

  RADIATION VALUES INPUT EVERY 10 MIN.
```

PBMMET OUTPUT

HOURLY SURFACE METEOROLOGICAL DATA

| HOUR | WIND SPEED (METERS/SEC) | TEMPERATURE (DEG.-C) |
|---|---|---|
| 5- 6 | 1.58 | 11.10 |
| 6- 7 | 1.68 | 11.60 |
| 7- 8 | 1.51 | 14.50 |
| 8- 9 | .86 | 17.80 |
| 9-10 | .39 | 20.80 |
| 10-11 | .39 | 23.50 |
| 11-12 | .80 | 25.50 |
| 12-13 | .09 | 26.90 |
| 13-14 | .48 | 27.80 |
| 14-15 | .71 | 28.50 |
| 15-16 | .79 | 28.70 |
| 16-17 | .89 | 28.20 |
| 17-18 | .90 | 26.10 |

INPUT VALUES FOR 'CHARACTERISTIC CURVE' MIX. HT. CALCULATIONS:

HMIN1 = 100.00 HMAX = 532.00 HMIN2 = 100.00 METERS

INPUT VALUES OF TOTAL SOLAR RADIATION:

| TIME (MIN. AFTER 0500 LST) | RAD. (LY/MIN) |
|---|---|
| 0 | .0000 |
| 10 | .0000 |
| 20 | .0000 |
| 30 | .0000 |
| 40 | .0000 |
| 50 | .0000 |
| 60 | .0000 |
| 70 | .5900-002 |
| 80 | .2540-001 |
| 90 | .5560-001 |
| 100 | .9360-001 |
| 110 | .1308+000 |
| 120 | .1739+000 |
| 130 | .2178+000 |
| 140 | .2647+000 |
| 150 | .3086+000 |
| 160 | .3512+000 |
| 170 | .3954+000 |
| 180 | .4414+000 |
| 190 | .4872+000 |
| 200 | .5311+000 |
| 210 | .5671+000 |
| 220 | .6034+000 |
| 230 | .6390+000 |
| 240 | .6788+000 |
| 250 | .7141+000 |
| 260 | .7507+000 |
| 270 | .7825+000 |
| 280 | .8146+000 |
| 290 | .8374+000 |
| 300 | .8659+000 |
| 310 | .8933+000 |
| 320 | .9152+000 |
| 330 | .9368+000 |
| 340 | .9504+000 |
| 350 | .9689+000 |
| 360 | .9783+000 |
| 370 | .9925+000 |
| 380 | .1009+001 |
| 390 | .1009+001 |
| 400 | .1020+001 |
| 410 | .1008+001 |
| 420 | .1009+001 |
| 430 | .9914+000 |
| 440 | .9824+000 |
| 450 | .9796+000 |
| 460 | .9813+000 |
| 470 | .9764+000 |
| 480 | .9582+000 |
| 490 | .9374+000 |
| 500 | .9101+000 |
| 510 | .8843+000 |
| 520 | .8555+000 |

| | |
|---|---|
| 530 | .8301+000 |
| 540 | .7981+000 |
| 550 | .7687+000 |
| 560 | .7289+000 |
| 570 | .6871+000 |
| 580 | .6533+000 |
| 590 | .6162+000 |
| 600 | .5854+000 |
| 610 | .5471+000 |
| 620 | .5074+000 |
| 630 | .4684+000 |
| 640 | .4232+000 |
| 650 | .3774+000 |
| 660 | .3344+000 |
| 670 | .2957+000 |
| 680 | .2533+000 |
| 690 | .2163+000 |
| 700 | .1802+000 |
| 710 | .1406+000 |
| 720 | .1015+000 |
| 730 | .6420-001 |
| 740 | .3190-001 |
| 750 | .8300-002 |
| 760 | .0000 |
| 770 | .0000 |
| 780 | .0000 |

INTERPOLATED MIXING HEIGHTS AND PHOTOLYTIC RATE CONSTANTS:

| TIME (LST) | MIX. HT (M) | RATE CONSTANTS : K (ATTENUATED) (/MIN) (K (CLEAR-SKY)) | | | | | |
|---|---|---|---|---|---|---|---|
| | | K( 1) | K( 2) | K( 3) | K( 4) | K( 5) | K( 6) |
| | | K( 7) | K( 8) | K( 9) | K(10) | K(11) | |
| 500. | 100.00 | .000 | .000 | .000 | .000 | .000 | .000 |
| | | (-.176+000) | (-.183-003) | (-.334-001) | (-.132-003) | (-.667-003) | (-.361-003) |
| | | .000 | .000 | .000 | .000 | .000 | |
| | | (-.691-004) | (-.706-003) | (-.706-003) | (-.168-002) | (-.168-002) | |
| 510. | 100.00 | .000 | .000 | .000 | .000 | .000 | .000 |
| | | (-.141+000) | (-.130-003) | (-.264-001) | (-.859-004) | (-.516-003) | (-.274-003) |
| | | .000 | .000 | .000 | .000 | .000 | |
| | | (-.514-004) | (-.566-003) | (-.566-003) | (-.134-002) | (-.134-002) | |
| 520. | 100.00 | .000 | .000 | .000 | .000 | .000 | .000 |
| | | (-.111+000) | (-.892-004) | (-.204-001) | (-.511-004) | (-.390-003) | (-.202-003) |
| | | .000 | .000 | .000 | .000 | .000 | |
| | | (-.371-004) | (-.442-003) | (-.442-003) | (-.105-002) | (-.105-002) | |
| 530. | 100.00 | .000 | .000 | .000 | .000 | .000 | .000 |
| | | (-.833-001) | (-.583-004) | (-.151-001) | (-.261-004) | (-.283-003) | (-.143-003) |
| | | .000 | .000 | .000 | .000 | .000 | |
| | | (-.258-004) | (-.333-003) | (-.333-003) | (-.792-003) | (-.792-003) | |
| 540. | 100.00 | .000 | .000 | .000 | .000 | .000 | .000 |
| | | (-.590-001) | (-.357-004) | (-.105-001) | (-.920-005) | (-.193-003) | (-.964-004) |
| | | .000 | .000 | .000 | .000 | .000 | |
| | | (-.170-004) | (-.236-003) | (-.236-003) | (-.561-003) | (-.561-003) | |
| 550. | 100.00 | .000 | .000 | .000 | .000 | .000 | .000 |
| | | (-.372-001) | (-.198-004) | (-.644-002) | ( .112-005) | (-.118-003) | (-.588-004) |
| | | .000 | .000 | .000 | .000 | .000 | |
| | | (-.103-004) | (-.149-003) | (-.149-003) | (-.353-003) | (-.353-003) | |
| 600. | 100.00 | .000 | .000 | .000 | .000 | .000 | .000 |
| | | (-.171-001) | (-.900-005) | (-.279-002) | ( .648-005) | (-.524-004) | (-.283-004) |
| | | .000 | .000 | .000 | .000 | .000 | |
| | | (-.501-005) | (-.686-004) | (-.686-004) | (-.163-003) | (-.163-003) | |
| 610. | 100.00 | .161-002 | .000 | .569-003 | .850-005 | .589-005 | .000 |
| | | ( .161-002) | (-.164-005) | ( .569-003) | ( .850-005) | ( .589-005) | (-.250-005) |
| | | .000 | .644-005 | .644-005 | .153-004 | .153-004 | |
| | | (-.781-006) | ( .644-005) | ( .644-005) | ( .153-004) | ( .153-004) | |
| 620. | 100.29 | .109-001 | .217-005 | .209-002 | .486-005 | .334-004 | .115-004 |
| | | ( .197-001) | ( .392-005) | ( .378-002) | ( .878-005) | ( .604-004) | ( .208-004) |
| | | .161-005 | .436-004 | .436-004 | .103-003 | .103-003 | |
| | | ( .290-005) | ( .787-004) | ( .787-004) | ( .187-003) | ( .187-003) | |
| 630. | 101.24 | .243-001 | .601-005 | .451-002 | .575-005 | .739-004 | .283-004 |
| | | ( .376-001) | ( .929-005) | ( .697-002) | ( .889-005) | ( .114-003) | ( .437-004) |
| | | .422-005 | .973-004 | .973-004 | .231-003 | .231-003 | |
| | | ( .652-005) | ( .150-003) | ( .150-003) | ( .357-003) | ( .357-003) | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 640. | 102.96 | .412-001 | .118-004 | .754-002 | .765-005 | .126-003 | .504-004 |
| | | ( .560-001) | ( .161-004) | ( .103-001) | ( .104-004) | ( .171-003) | ( .685-004) |
| | | .776-005 | .165-003 | .165-003 | .391-003 | .391-003 | |
| | | ( .105-004) | ( .224-003) | ( .224-003) | ( .532-003) | ( .532-003) | |
| 650. | 105.54 | .576-001 | .197-004 | .105-001 | .113-004 | .178-003 | .745-004 |
| | | ( .753-001) | ( .257-004) | ( .138-001) | ( .148-004) | ( .233-003) | ( .973-004) |
| | | .118-004 | .230-003 | .230-003 | .547-003 | .547-003 | |
| | | ( .154-004) | ( .301-003) | ( .301-003) | ( .715-003) | ( .715-003) | |
| 700. | 109.11 | .765-001 | .317-004 | .140-001 | .187-004 | .242-003 | .105-003 |
| | | ( .961-001) | ( .398-004) | ( .176-001) | ( .235-004) | ( .304-003) | ( .132-003) |
| | | .172-004 | .306-003 | .306-003 | .727-003 | .727-003 | |
| | | ( .216-004) | ( .384-003) | ( .384-003) | ( .913-003) | ( .913-003) | |
| 710. | 113.77 | .956-001 | .480-004 | .176-001 | .303-004 | .311-003 | .140-003 |
| | | ( .119+000) | ( .597-004) | ( .219-001) | ( .377-004) | ( .386-003) | ( .174-003) |
| | | .237-004 | .382-003 | .382-003 | .908-003 | .908-003 | |
| | | ( .295-004) | ( .475-003) | ( .475-003) | ( .113-002) | ( .113-002) | |
| 720. | 119.64 | .116+000 | .696-004 | .215-001 | .457-004 | .388-003 | .181-003 |
| | | ( .143+000) | ( .859-004) | ( .265-001) | ( .564-004) | ( .478-003) | ( .224-003) |
| | | .316-004 | .463-003 | .463-003 | .110-002 | .110-002 | |
| | | ( .390-004) | ( .572-003) | ( .572-003) | ( .136-002) | ( .136-002) | |
| 730. | 126.85 | .135+000 | .954-004 | .251-001 | .624-004 | .463-003 | .224-003 |
| | | ( .167+000) | ( .119-003) | ( .312-001) | ( .777-004) | ( .577-003) | ( .279-003) |
| | | .402-004 | .538-003 | .538-003 | .128-002 | .128-002 | |
| | | ( .500-004) | ( .670-003) | ( .670-003) | ( .159-002) | ( .159-002) | |
| 740. | 135.50 | .153+000 | .126-003 | .286-001 | .794-004 | .541-003 | .270-003 |
| | | ( .191+000) | ( .158-003) | ( .359-001) | ( .995-004) | ( .678-003) | ( .338-003) |
| | | .496-004 | .611-003 | .611-003 | .145-002 | .145-002 | |
| | | ( .621-004) | ( .765-003) | ( .765-003) | ( .182-002) | ( .182-002) | |
| 750. | 145.74 | .171+000 | .164-003 | .323-001 | .962-004 | .624-003 | .321-003 |
| | | ( .214+000) | ( .205-003) | ( .404-001) | ( .120-003) | ( .779-003) | ( .400-003) |
| | | .603-004 | .686-003 | .686-003 | .163-002 | .163-002 | |
| | | ( .752-004) | ( .856-003) | ( .856-003) | ( .203-002) | ( .203-002) | |
| 800. | 157.56 | .192+000 | .211-003 | .364-001 | .113-003 | .718-003 | .379-003 |
| | | ( .236+000) | ( .259-003) | ( .448-001) | ( .139-003) | ( .883-003) | ( .467-003) |
| | | .728-004 | .768-003 | .768-003 | .182-002 | .182-002 | |
| | | ( .896-004) | ( .945-003) | ( .945-003) | ( .224-002) | ( .224-002) | |
| 810. | 170.80 | .213+000 | .266-003 | .406-001 | .130-003 | .818-003 | .443-003 |
| | | ( .258+000) | ( .322-003) | ( .491-001) | ( .157-003) | ( .988-003) | ( .536-003) |
| | | .868-004 | .853-003 | .853-003 | .202-002 | .202-002 | |
| | | ( .105-003) | ( .103-002) | ( .103-002) | ( .245-002) | ( .245-002) | |
| 820. | 185.25 | .233+000 | .328-003 | .447-001 | .147-003 | .918-003 | .510-003 |
| | | ( .277+000) | ( .390-003) | ( .531-001) | ( .174-003) | ( .109-002) | ( .605-003) |
| | | .102-003 | .934-003 | .934-003 | .222-002 | .222-002 | |
| | | ( .121-003) | ( .111-002) | ( .111-002) | ( .263-002) | ( .263-002) | |
| 830. | 200.69 | .250+000 | .392-003 | .481-001 | .162-003 | .101-002 | .571-003 |
| | | ( .295+000) | ( .462-003) | ( .568-001) | ( .191-003) | ( .119-002) | ( .674-003) |

| | | |
|---|---|---|
| | | .116-003 .100-002 .100-002 .238-002 .238-002<br>( .136-003) ( .118-002) ( .118-002) ( .281-002) ( .281-002) |
| 840. | 216.92 | .267+000 .461-003 .515-001 .177-003 .110-002 .634-003<br>( .312+000) ( .539-003) ( .603-001) ( .207-003) ( .128-002) ( .742-003)<br>.130-003 .107-002 .107-002 .254-002 .254-002<br>( .152-003) ( .125-002) ( .125-002) ( .296-002) ( .296-002) |
| 850. | 233.73 | .283+000 .535-003 .548-001 .193-003 .118-002 .698-003<br>( .327+000) ( .619-003) ( .634-001) ( .223-003) ( .137-002) ( .807-003)<br>.145-003 .113-002 .113-002 .269-002 .269-002<br>( .168-003) ( .131-002) ( .131-002) ( .311-002) ( .311-002) |
| 900. | 250.91 | .301+000 .617-003 .585-001 .210-003 .128-002 .767-003<br>( .341+000) ( .700-003) ( .664-001) ( .238-003) ( .145-002) ( .870-003)<br>.161-003 .120-002 .120-002 .286-002 .286-002<br>( .183-003) ( .137-002) ( .137-002) ( .324-002) ( .324-002) |
| 910. | 268.26 | .317+000 .700-003 .618-001 .226-003 .137-002 .832-003<br>( .354+000) ( .782-003) ( .690-001) ( .253-003) ( .153-002) ( .930-003)<br>.177-003 .127-002 .127-002 .301-002 .301-002<br>( .198-003) ( .142-002) ( .142-002) ( .336-002) ( .336-002) |
| 920. | 285.57 | .333+000 .788-003 .651-001 .243-003 .146-002 .899-003<br>( .366+000) ( .865-003) ( .715-001) ( .267-003) ( .160-002) ( .987-003)<br>.193-003 .133-002 .133-002 .316-002 .316-002<br>( .212-003) ( .146-002) ( .146-002) ( .347-002) ( .347-002) |
| 930. | 302.64 | .347+000 .874-003 .680-001 .259-003 .154-002 .969-003<br>( .376+000) ( .947-003) ( .737-001) ( .280-003) ( .167-002) ( .104-002)<br>.208-003 .139-002 .139-002 .330-002 .330-002<br>( .226-003) ( .150-002) ( .150-002) ( .357-002) ( .357-002) |
| 940. | 319.24 | .361+000 .962-003 .709-001 .274-003 .162-002 .102-002<br>( .386+000) ( .103-002) ( .757-001) ( .293-003) ( .173-002) ( .109-002)<br>.224-003 .145-002 .145-002 .343-002 .343-002<br>( .239-003) ( .154-002) ( .154-002) ( .366-002) ( .366-002) |
| 950. | 335.19 | .371+000 .104-002 .730-001 .286-003 .168-002 .107-002<br>( .394+000) ( .111-002) ( .775-001) ( .304-003) ( .178-002) ( .114-002)<br>.236-003 .149-002 .149-002 .353-002 .353-002<br>( .251-003) ( .158-002) ( .158-002) ( .374-002) ( .374-002) |
| 1000. | 350.26 | .384+000 .113-002 .756-001 .300-003 .175-002 .113-002<br>( .402+000) ( .118-002) ( .791-001) ( .314-003) ( .183-002) ( .118-002)<br>.251-003 .154-002 .154-002 .365-002 .365-002<br>( .262-003) ( .161-002) ( .161-002) ( .382-002) ( .382-002) |
| 1010. | 364.30 | .396+000 .121-002 .781-001 .314-003 .183-002 .118-002<br>( .409+000) ( .125-002) ( .806-001) ( .324-003) ( .188-002) ( .122-002)<br>.265-003 .158-002 .158-002 .376-002 .376-002<br>( .273-003) ( .163-002) ( .163-002) ( .388-002) ( .388-002) |
| 1020. | 377.32 | .406+000 .129-002 .802-001 .326-003 .188-002 .123-002<br>( .416+000) ( .132-002) ( .821-001) ( .334-003) ( .193-002) ( .126-002)<br>.277-003 .162-002 .162-002 .386-002 .386-002<br>( .284-003) ( .166-002) ( .166-002) ( .395-002) ( .395-002) |

| | | | | | | |
|---|---|---|---|---|---|---|
| 1030. | 389.41 | .416+000 | .137-002 | .822-001 | .338-003 | .194-002 | .128-002 |
| | | ( .422+000) | ( .139-002) | ( .834-001) | ( .342-003) | ( .197-002) | ( .130-002) |
| | | | .289-003 | .166-002 | .166-002 | .395-002 | .395-002 |
| | | | ( .293-003) | ( .169-002) | ( .169-002) | ( .401-002) | ( .401-002) |
| 1040. | 400.63 | .421+000 | .143-002 | .833-001 | .345-003 | .198-002 | .131-002 |
| | | ( .427+000) | ( .145-002) | ( .845-001) | ( .350-003) | ( .201-002) | ( .133-002) |
| | | | .297-003 | .168-002 | .168-002 | .400-002 | .400-002 |
| | | | ( .302-003) | ( .171-002) | ( .171-002) | ( .406-002) | ( .406-002) |
| 1050. | 411.06 | .429+000 | .149-002 | .849-001 | .354-003 | .203-002 | .135-002 |
| | | ( .431+000) | ( .150-002) | ( .854-001) | ( .356-003) | ( .204-002) | ( .136-002) |
| | | | .307-003 | .172-002 | .172-002 | .407-002 | .407-002 |
| | | | ( .309-003) | ( .173-002) | ( .173-002) | ( .410-002) | ( .410-002) |
| 1100. | 420.77 | .433+000 | .154-002 | .858-001 | .360-003 | .205-002 | .137-002 |
| | | ( .435+000) | ( .155-002) | ( .862-001) | ( .362-003) | ( .207-002) | ( .138-002) |
| | | | .314-003 | .173-002 | .173-002 | 411-002 | .411-002 |
| | | | ( .316-003) | ( .174-002) | ( .174-002) | ( .413-002) | ( .413-002) |
| 1110. | 429.84 | .438+000 | .159-002 | .869-001 | .367-003 | .209-002 | .140-002 |
| | | ( .438+000) | ( .159-002) | ( .869-001) | ( .367-003) | ( .209-002) | ( .140-002) |
| | | | .321-003 | .175-002 | .175-002 | .416-002 | .416-002 |
| | | | ( .321-003) | ( .175-002) | ( .175-002) | ( .416-002) | ( .416-002) |
| 1120. | 438.33 | .441+000 | .162-002 | .874-001 | .370-003 | .211-002 | .141-002 |
| | | ( .441+000) | ( .162-002) | ( .874-001) | ( .370-003) | ( .211-002) | ( .141-002) |
| | | | .325-003 | .176-002 | .176-002 | .419-002 | .419-002 |
| | | | ( .325-003) | ( .176-002) | ( .176-002) | ( .419-002) | ( .419-002) |
| 1130. | 446.32 | .443+000 | .164-002 | .878-001 | .373-003 | .212-002 | .143-002 |
| | | ( .443+000) | ( .164-002) | ( .878-001) | ( .373-003) | ( .212-002) | ( .143-002) |
| | | | .328-003 | .177-002 | .177-002 | .421-002 | .421-002 |
| | | | ( .328-003) | ( .177-002) | ( .177-002) | ( .421-002) | ( .421-002) |
| 1140. | 453.88 | .444+000 | .165-002 | .881-001 | .375-003 | .213-002 | .143-002 |
| | | ( .444+000) | ( .165-002) | ( .881-001) | ( .375-003) | ( .213-002) | ( .143-002) |
| | | | .330-003 | .178-002 | .178-002 | .422-002 | .422-002 |
| | | | ( .330-003) | ( .178-002) | ( .178-002) | ( .422-002) | ( .422-002) |
| 1150. | 461.09 | .445+000 | .166-002 | .883-001 | .376-003 | .213-002 | .144-002 |
| | | ( .445+000) | ( .166-002) | ( .883-001) | ( .376-003) | ( .213-002) | ( .144-002) |
| | | | .331-003 | .178-002 | .178-002 | .423-002 | .423-002 |
| | | | ( .331-003) | ( .178-002) | ( .178-002) | ( .423-002) | ( .423-002) |
| 1200. | 468.02 | .445+000 | .166-002 | .883-001 | .376-003 | .213-002 | .144-002 |
| | | ( .445+000) | ( .166-002) | ( .883-001) | ( .376-003) | ( .213-002) | ( .144-002) |
| | | | .331-003 | .178-002 | .178-002 | .423-002 | .423-002 |
| | | | ( .331-003) | ( .178-002) | ( .178-002) | ( .423-002) | ( .423-002) |
| 1210. | 474.72 | .441+000 | .163-002 | .875-001 | .372-003 | .211-002 | .142-002 |
| | | ( .445+000) | ( .165-002) | ( .882-001) | ( .375-003) | ( .213-002) | ( .143-002) |
| | | | .327-003 | .176-002 | .176-002 | .419-002 | .419-002 |
| | | | ( .330-003) | ( .178-002) | ( .178-002) | ( .422-002) | ( .422-002) |
| 1220. | 481.17 | .438+000 | .161-002 | .868-001 | .368-003 | .209-002 | .141-002 |

```
                ( .444+000) ( .163-002) ( .880-001) ( .373-003) ( .212-002) ( .143-002)
                      .323-003    .175-002    .175-002    .416-002    .416-002
                   ( .328-003) ( .177-002) ( .177-002) ( .421-002) ( .421-002)

1230.   487.37     .437+000    .159-002    .868-001    .367-003    .209-002    .140-002
                ( .442+000) ( .160-002) ( .877-001) ( .370-003) ( .211-002) ( .141-002)
                      .321-003    .175-002    .175-002    .416-002    .416-002
                   ( .324-003) ( .177-002) ( .177-002) ( .420-002) ( .420-002)

1240.   493.28     .439+000    .157-002    .871-001    .366-003    .209-002    .140-002
                ( .440+000) ( .157-002) ( .872-001) ( .367-003) ( .209-002) ( .140-002)
                      .320-003    .176-002    .176-002    .417-002    .417-002
                   ( .320-003) ( .176-002) ( .176-002) ( .418-002) ( .418-002)

1250.   498.89     .437+000    .153-002    .867-001    .362-003    .207-002    .138-002
                ( .437+000) ( .153-002) ( .867-001) ( .362-003) ( .207-002) ( .138-002)
                      .315-003    .175-002    .175-002    .415-002    .415-002
                   ( .315-003) ( .175-002) ( .175-002) ( .415-002) ( .415-002)

1300.   504.18     .432+000    .147-002    .856-001    .355-003    .204-002    .135-002
                ( .434+000) ( .148-002) ( .859-001) ( .357-003) ( .205-002) ( .136-002)
                      .307-003    .173-002    .173-002    .410-002    .410-002
                   ( .308-003) ( .174-002) ( .174-002) ( .412-002) ( .412-002)

1310.   509.12     .424+000    .141-002    .840-001    .346-003    .199-002    .131-002
                ( .430+000) ( .143-002) ( .851-001) ( .351-003) ( .202-002) ( .133-002)
                      .297-003    .170-002    .170-002    .403-002    .403-002
                   ( .301-003) ( .172-002) ( .172-002) ( .408-002) ( .408-002)

1320.   513.69     .414+000    .133-002    .819-001    .334-003    .193-002    .127-002
                ( .425+000) ( .136-002) ( .841-001) ( .343-003) ( .198-002) ( .130-002)
                      .285-003    .166-002    .166-002    .393-002    .393-002
                   ( .292-003) ( .170-002) ( .170-002) ( .404-002) ( .404-002)

1330.   517.88     .404+000    .125-002    .798-001    .323-003    .187-002    .122-002
                ( .420+000) ( .130-002) ( .829-001) ( .335-003) ( .194-002) ( .127-002)
                      .272-003    .162-002    .162-002    .384-002    .384-002
                   ( .283-003) ( .168-002) ( .168-002) ( .399-002) ( .399-002)

1340.   521.66     .392+000    .116-002    .773-001    .309-003    .180-002    .116-002
                ( .414+000) ( .123-002) ( .816-001) ( .326-003) ( .190-002) ( .123-002)
                      .258-003    .157-002    .157-002    .372-002    .372-002
                   ( .273-003) ( .165-002) ( .165-002) ( .393-002) ( .393-002)

1350.   525.02     .381+000    .108-002    .751-001    .296-003    .174-002    .111-002
                ( .407+000) ( .115-002) ( .802-001) ( .316-003) ( .185-002) ( .119-002)
                      .245-003    .152-002    .152-002    .362-002    .362-002
                   ( .261-003) ( .163-002) ( .163-002) ( .386-002) ( .386-002)

1400.   527.92     .368+000    .989-003    .723-001    .281-003    .166-002    .105-002
                ( .399+000) ( .107-002) ( .785-001) ( .305-003) ( .180-002) ( .114-002)
                      .230-003    .147-002    .147-002    .349-002    .349-002
                   ( .249-003) ( .160-002) ( .160-002) ( .379-002) ( .379-002)

1410.   530.35     .352+000    .893-003    .691-001    .264-003    .157-002    .982-003
                ( .390+000) ( .992-003) ( .766-001) ( .293-003) ( .174-002) ( .109-002)
                      .213-003    .141-002    .141-002    .334-002    .334-002
```

( .237-003) ( .156-002) ( .156-002) ( .371-002) ( .371-002)

1420. 532.00 .338+000 .807-003 .663-001 .249-003 .149-002 .922-003
( .381+000) ( .908-003) ( .746-001) ( .280-003) ( .168-002) ( .104-002)
.198-003 .135-002 .135-002 .321-002 .321-002
( .223-003) ( .152-002) ( .152-002) ( .362-002) ( .362-002)

1430. 532.00 .320+000 .713-003 .626-001 .231-003 .139-002 .849-003
( .370+000) ( .824-003) ( .723-001) ( .267-003) ( .161-002) ( .980-003)
.181-003 .128-002 .128-002 .304-002 .304-002
( .209-003) ( .148-002) ( .148-002) ( .352-002) ( .352-002)

1440. 532.00 .306+000 .631-003 .596-001 .215-003 .131-002 .786-003
( .358+000) ( .740-003) ( .698-001) ( .252-003) ( .153-002) ( .921-003)
.165-003 .122-002 .122-002 .291-002 .291-002
( .194-003) ( .143-002) ( .143-002) ( .340-002) ( .340-002)

1450. 532.00 .290+000 .551-003 .563-001 .199-003 .122-002 .720-003
( .345+000) ( .656-003) ( .671-001) ( .237-003) ( .146-002) ( .858-003)
.150-003 .116-002 .116-002 .275-002 .275-002
( .178-003) ( .138-002) ( .138-002) ( .328-002) ( .328-002)

1500. 532.00 .277+000 .480-003 .536-001 .185-003 .114-002 .662-003
( .331+000) ( .574-003) ( .641-001) ( .221-003) ( .137-002) ( .792-003)
.136-003 .111-002 .111-002 .263-002 .263-002
( .163-003) ( .133-002) ( .133-002) ( .315-002) ( .315-002)

1510. 532.00 .260+000 .408-003 .502-001 .168-003 .105-002 .597-003
( .316+000) ( .495-003) ( .609-001) ( .204-003) ( .128-002) ( .724-003)
.121-003 .104-002 .104-002 .247-002 .247-002
( .146-003) ( .126-002) ( .126-002) ( .300-002) ( .300-002)

1520. 532.00 .243+000 .341-003 .466-001 .152-003 .961-003 .532-003
( .299+000) ( .419-003) ( .574-001) ( .187-003) ( .118-002) ( .655-003)
.106-003 .972-003 .972-003 .231-002 .231-002
( .130-003) ( .120-002) ( .120-002) ( .284-002) ( .284-002)

1530. 532.00 .226+000 .280-003 .431-001 .136-003 .870-003 .471-003
( .280+000) ( .348-003) ( .536-001) ( .169-003) ( .108-002) ( .584-003)
.919-004 .903-003 .903-003 .215-002 .215-002
( .114-003) ( .112-002) ( .112-002) ( .266-002) ( .266-002)

1540. 532.00 .206+000 .223-003 .391-001 .119-003 .770-003 .406-003
( .260+000) ( .283-003) ( .494-001) ( .151-003) .975-003) ( .513-003)
.777-004 .822-003 .822-003 .195-002 .195-002
( .983-004) ( .104-002) ( .104-002) ( .247-002) ( .247-002)

1550. 532.00 .185+000 .174-003 .349-001 .102-003 .672-003 .344-003
( .238+000) ( .224-003) ( .449-001) ( .132-003) ( .865-003) ( .443-003)
.645-004 .739-003 .739-003 .176-002 .176-002
( .830-004) ( .951-003) ( .951-003) ( .226-002) ( .226-002)

1600. 532.00 .165+000 .133-003 .310-001 .866-004 .582-003 .290-003
( .213+000) ( .172-003) ( .400-001) ( .112-003) ( .752-003) ( .374-003)
.530-004 .661-003 .661-003 .157-002 .157-002
( .684-004) ( .853-003) ( .853-003) ( .203-002) ( .203-002)

1610. 532.00

.148+000 .101-003 .275-001 .724-004 .503-003 .242-003
( .187+000) ( .128-003) ( .348-001) ( .918-004) ( .638-003) ( .307-003)
.432-004 .591-003 .591-003 .140-002 .140-002
( .548-004) ( .749-003) ( .749-003) ( .178-002) ( .178-002)

1620. 532.00

.128+000 .732-004 .236-001 .581-004 .421-003 .195-003
( .160+000) ( .918-004) ( .296-001) ( .728-004) ( .527-003) ( .245-003)
.339-004 .512-003 .512-003 .122-002 .122-002
( .425-004) ( .642-003) ( .642-003) ( .152-002) ( .152-002)

1630. 532.00

.110+000 .521-004 .202-001 .460-004 .350-003 .156-003
( .134+000) ( .630-004) ( .244-001) ( .557-004) ( .424-003) ( .189-003)
.263-004 .442-003 .442-003 .105-002 .105-002
( .319-004) ( .535-003) ( .535-003) ( .127-002) ( .127-002)

1640. 525.31

.927-001 .356-004 .168-001 .354-004 .284-003 .122-003
( .108+000) ( .415-004) ( .196-001) ( .413-004) ( .332-003) ( .142-003)
.198-004 .371-003 .371-003 .881-003 .881-003
( .232-004) ( .433-003) ( .433-003) ( .103-002) ( .103-002)

1650. 494.34

.719-001 .227-004 .130-001 .256-004 .216-003 .888-004
( .836-001) ( .263-004) ( .151-001) ( .297-004) ( .251-003) ( .103-003)
.140-004 .288-003 .288-003 .683-003 .683-003
( .163-004) ( .335-003) ( .335-003) ( .795-003) ( .795-003)

1700. 463.38

.512-001 .136-004 .928-002 .175-004 .152-003 .601-004
( .606-001) ( .161-004) ( .110-001) ( .208-004) ( .180-003) ( .712-004)
.917-005 .205-003 .205-003 .486-003 .486-003
( .109-004) ( .242-003) ( .242-003) ( .576-003) ( .576-003)

1710. 432.42

.314-001 .735-005 .579-002 .112-004 .936-004 .353-004
( .388-001) ( .907-005) ( .714-002) ( .138-004) ( .116-003) ( .436-004)
.522-005 .126-003 .126-003 .298-003 .298-003
( .645-005) ( .155-003) ( .155-003) ( .368-003) ( .368-003)

1720. 401.45

.145-001 .275-005 .282-002 .651-005 .448-004 .148-004
( .178-001) ( .337-005) ( .346-002) ( .799-005) ( .550-004) ( .182-004)
.202-005 .579-004 .579-004 .138-003 .138-003
( .248-005) ( .710-004) ( .710-004) ( .169-003) ( .169-003)

1730. 370.49

.000 .000 .000 .000 .000 .000
(-.275-002) (-.275-005) (-.159-003) ( .255-005) (-.531-005) (-.737-005)
.000 .000 .000 .000 .000
(-.157-005) (-.110-004) (-.110-004) (-.261-004) (-.261-004)

1740. 339.53

.000 .000 .000 .000 .000 .000
(-.235-001) (-.110-004) (-.386-002) (-.355-005) (-.690-004) (-.356-004)
.000 .000 .000 .000 .000
(-.623-005) (-.939-004) (-.939-004) (-.223-003) (-.223-003)

1750. 314.60

.000 .000 .000 .000 .000 .000
(-.453-001) (-.233-004) (-.785-002) (-.117-004) (-.140-003) (-.693-004)
.000 .000 .000 .000 .000
(-.121-004) (-.181-003) (-.181-003) (-.431-003) (-.431-003)

1800. 308.78

.000 .000 .000 .000 .000 .000
(-.691-001) (-.413-004) (-.123-001) (-.238-004) (-.224-003) (-.111-003)
.000 .000 .000 .000 .000
(-.196-004) (-.277-003) (-.277-003) (-.657-003) (-.657-003)

INPUT DATA - PBMAQE EXAMPLE PROBLEM

```
      AIR QUALITY AND EMISSIONS     ST. LOUIS  76275
          20.0      25.0
            6
            5
            1
            5          5
            1    1
            5    5    3
     CO  NO  NO2 O3  HO
     CO              1.6223
     NO               .1239
     NO2              .0391
     NMHC            1.1991
     O3               .0025
     H2O          7878.7730
     CO
       .66478  .94666  .88844  .80268  .81451  .80689  .06851  .27964  .31721  .42426
       .38884  .54567  .89854 2.20757 2.40522
     NO
       .04121  .03570  .03076  .01685  .01240  .00489  .00250  .00250  .00250  .00250
       .00255  .00261  .00298  .03592  .01368
     NO2
       .01933  .02250  .02729  .04307  .04161  .02248  .00979  .00783  .00936  .00342
       .02562  .02373  .03179  .05614  .06787
     NMHC
       .60496  .52997  .30059  .29770  .28063  .28063  .21800  .15500  .14700  .17874
       .27979  .27674  .40058  .44804  .81160
     O3
       .01018  .00505  .01328  .02404  .03312  .05421  .08282  .10150  .10375  .12857
       .13818  .14391  .11388  .10320  .09493
     O3
       .06300  .06300  .06300  .06300  .06300  .06300  .06300  .06300  .06300  .06300
       .06300  .06300  .06300  .06300  .06300
     CO
      1.77063 3.30528 4.01328 3.46760 2.69850 2.29946 2.12176 1.48728 1.36505 1.38847
      1.40420 1.62544 2.92169 5.76281 7.84034
     NO
       .12960  .18725  .16782  .10554  .03489  .01420  .00651  .00296  .00298  .00273
       .00276  .00380  .02440  .06017  .11055
     NO2
       .03824  .04084  .05692  .08629  .10230  .09985  .08254  .05818  .05340  .05142
       .05671  .06103  .10773  .16397  .16908
     NMHC
      1.20173 1.35853 1.48753 1.20917  .99288  .95591  .96199  .59593  .48726  .53084
       .53538  .58416 1.03837 2.28581 2.91273
     O3
       .00250  .00250  .00271  .00701  .03225  .06871  .10298  .13461  .15853  .18320
       .18078  .16096  .08373  .01287  .01084
     CO
      41741.79  72303.22  65620.24  37965.50  37311.44  39966.64  41547.18  40442.05
      43707.63  50127.14  61928.40  57936.70  36420.60
     NOX
       4924.99   7217.68   7270.63   6224.52   6057.58   6287.49   6465.04   6339.62
       6712.68   7449.48   7414.50   7067.02   3770.49
     THC
       9771.36  13836.15  14863.21  11771.58  11668.45  12069.51  12295.97  12143.83
```

INPUT DATA - PBMAQE EXAMPLE PROBLEM

```
     12620.04  13714.90  15035.52   8548.48   6399.18
HC0
  58282.83  86591.98  78273.55  55688.74  53961.63  56016.37  57643.76  56539.04
  59870.05  66573.90  76041.83  56501.06  41390.16
HC1
  38788.37  62325.80  54292.58  36443.51  35828.05  38174.78  39541.86  38628.43
  41433.05  47186.80  55084.16  45865.09  32582.54
HC2
  52702.99  75766.95  81009.75  63490.92  63210.23  65640.60  66926.97  66066.33
  68787.98  75366.50  82637.54  46592.41  35838.98
HC3
  13972.26  19519.45  19183.75  14945.35  14764.24  15292.28  15616.36  15399.65
  16060.28  17382.19  19257.15  12828.51   9115.62
HC4
  15851.06  22445.79  26167.54  21256.50  21095.89  21769.87  22127.62  21887.91
  22645.74  24462.51  26629.47  13949.07  10513.27
CO
   7915.04   7922.14   7931.76   7940.81   7944.19   7932.51   7930.35   7934.00
   7941.62   7941.66   7933.38   7933.58   7934.12
NOX
   1367.89   1499.07   1671.33   1821.69   1845.21   1685.55   1645.74   1710.05
   1820.21   1828.15   1695.69   1701.91   1710.29
THC
   1902.87   1904.82   3365.71   3368.31   3368.95   3365.87   3365.22   3366.33
   3368.43   3368.38   3366.18   3343.57   3343.75
HC0
   7963.88   8034.24  10604.99  10698.35  10721.58  10610.57  10587.33  1062[illegible].30
  10702.67  10700.84  10622.01  10600.06  10606.53
HC1
   2238.85   2241.20   2413.33   2416.45   2417.22   2413.52   2412.74   2414.08
   2416.59   2416.53   2413.90   2413.92   2414.14
HC2
   8148.96   8151.30  16522.59  16525.70  16526.48  16522.78  16522.00  16523.33
  16525.85  16525.79  16523.07  16344.39  16344.60
HC3
     33.19     35.53     38.86     41.97     42.74     39.04     38.27     39.60
     42.11     42.05     39.43     39.45     39.66
HC4
   6677.94   6678.72  11800.71  11801.75  11802.01  11800.77  11800.52  11800.96
  11801.80  11801.78  11800.88  11776.00  11776.08
**
```

PBMAQE -- AIR QUALITY/EMISSIONS PREPROCESSOR FOR THE PHOTOCHEMICAL BOX MODEL
**********
AIR QUALITY AND EMISSIONS ST. LOUIS 76275

SUMMARY OF CONTROLS:

NUMBER OF INITIAL CONDITION SPECIES SPECIFIED = 6

NUMBER OF TOP BOUNDARY CONDITION SPECIES SPECIFIED = 1

NUMBER OF LATERAL BOUNDARY CONDITION SPECIES SPECIFIED = 5

NUMBER OF OBSERVED SPECIES SPECIFIED = 5

NUMBER OF SPECIES SPECIFIED FOR PRINTER PLOTS = 5

DEFAULT HC SPECIATION FACTORS USED FOR INIT. NMHC =
.0440000 .0263000 .0394000 .0786000 .0608000 .0202000 .0149000 .0099000

DEFAULT HC SPECIATION FACTORS USED FOR BOUND. COND. NMHC =
.0440000 .0263000 .0394000 .0786000 .0608000 .0202000 .0149000 .0099000

DEFAULT HC SPECIATION FACTORS USED FOR OBSERVED NMHC =
.0440000 .0263000 .0394000 .0786000 .0608000 .0202000 .0149000 .0099000

SOURCE EMISSIONS ARE SPECIFIED

POINT SOURCES ARE SEPARATELY SPECIFIED

RATIO OF NO2/NOX IN AREA AND LINE SOURCES = .1000

RATIO OF NO2/NOX IN POINT SOURCES = .1000

RATIO OF CH4/THC IN AREA AND LINE SOURCES = .0000

RATIO OF CH4/THC IN POINT SOURCES = .0600

AIR QUALITY VALUES INPUT ON UNIT NUMBER 5

SOURCE EMISSIONS VALUES INPUT ON UNIT NUMBER 5

CARD-IMAGE OUTPUT DATA STORED ON UNIT NUMBER 3

SIZE OF HORIZONTAL SIDE OF PBM DOMAIN (KM) = 20.0000

AVERAGE AMBIENT TEMPERATURE DURING SIMULATION (DEG-C) = 25.0000

NUMBER OF HOURS OF DATA TO BE PROCESSED = 13

AIR QUALITY AND EMISSIONS  ST. LOUIS  76275

SPECIFIED INITIAL CONCENTRATIONS (FOR 0500 L.S.T.):

| SPECIES | CONCENTRATION (PPM) |
|---|---|
| CO | 1.622300 |
| NO | .123900 |
| NO2 | .039100 |
| NRHC | 1.199100 |
| NONR | .052760 |
| ETH | .031536 |
| OLE | .047245 |
| PAR | .094249 |
| FORM | .072905 |
| ALD | .024222 |
| ARO | .017867 |
| TOL | .011871 |
| O3 | .002500 |
| H2O | 7878.773010 |



AIR QUALITY AND EMISSIONS  ST. LOUIS  76275

TOP BOUNDARY CONCENTRATIONS:

| SPECIES | CONCENTRATIONS (PPM) DURING SPECIFIED HOURS (L.S.T.) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 5- 6 | 6- 7 | 7- 8 | 8- 9 | 9-10 | 10-11 | 11-12 | 12-13 | 13-14 | 14-15 |
| O3 | .6300-001 | .6300-001 | .6300-001 | .6300-001 | .6300-001 | .6300-001 | .6300-001 | .6300-001 | .6300-001 | .6300-001 |

| SPECIES | 15-16 | 16-17 | 17-18 |
|---|---|---|---|
| O3 | .6300-001 | .6300-001 | .6300-001 |

AIR QUALITY AND EMISSIONS ST. LOUIS 76275

LATERAL BOUNDARY CONCENTRATIONS:

| SPECIES | CONCENTRATIONS (PPM) DURING SPECIFIED HOURS (L.S.T.) 5- 6 | 6- 7 | 7- 8 | 8- 9 | 9-10 | 10-11 | 11-12 | 12-13 | 13-14 | 14-15 |
|---|---|---|---|---|---|---|---|---|---|---|
| CO | .6648+000 | .9467+000 | .8884+000 | .8027+000 | .8145+000 | .8069+000 | .6851-001 | .2796+000 | .3172+000 | .4243+000 |
| NO | .4121-001 | .3570-001 | .3076-001 | .1685-001 | .1240-001 | .4890-002 | .2500-002 | .2500-002 | .2500-002 | .2500-002 |
| NO2 | .1933-001 | .2250-001 | .2729-001 | .4307-001 | .4161-001 | .2248-001 | .9790-002 | .7830-002 | .9360-002 | .3420-002 |
| NMHC | .6050+000 | .5300+000 | .3006+000 | .2977+000 | .2806+000 | .2806+000 | .2180+000 | .1550+000 | .1470+000 | .1787+000 |
| NONR | .2662-001 | .2332-001 | .1323-001 | .1310-001 | .1235-001 | .1235-001 | .9592-002 | .6820-002 | .6468-002 | .7865-002 |
| ETH | .1591-001 | .1394-001 | .7906-002 | .7830-002 | .7381-002 | .7381-002 | .5733-002 | .4076-002 | .3866-002 | .4701-002 |
| OLE | .2384-001 | .2088-001 | .1184-001 | .1173-001 | .1106-001 | .1106-001 | .8589-002 | .6107-002 | .5792-002 | .7042-002 |
| PAR | .4755-001 | .4166-001 | .2363-001 | .2340-001 | .2206-001 | .2206-001 | .1713-001 | .1218-001 | .1155-001 | .1405-001 |
| FORM | .3678-001 | .3222-001 | .1828-001 | .1810-001 | .1706-001 | .1706-001 | .1325-001 | .9424-002 | .8938-002 | .1087-001 |
| ALD | .1222-001 | .1071-001 | .6072-002 | .6014-002 | .5669-002 | .5669-002 | .4404-002 | .3131-002 | .2969-002 | .3611-002 |
| ARO | .9014-002 | .7897-002 | .4479-002 | .4436-002 | .4181-002 | .4181-002 | .3248-002 | .2309-002 | .2190-002 | .2663-002 |
| TOL | .5989-002 | .5247-002 | .2976-002 | .2947-002 | .2778-002 | .2778-002 | .2158-002 | .1534-002 | .1455-002 | .1770-002 |
| O3 | .1018-001 | .5050-002 | .1328-001 | .2404-001 | .3312-001 | .5421-001 | .8282-001 | .1015+000 | .1037+000 | .1286+000 |

| SPECIES | 15-16 | 16-17 | 17-18 |
|---|---|---|---|
| CO | .3888+000 | .5457+000 | .8985+000 |
| NO | .2550-002 | .2610-002 | .2980-002 |
| NO2 | .2562-001 | .2373-001 | .3179-001 |
| NMHC | .2798+000 | .2767+000 | .4006+000 |
| NONR | .1231-001 | .1218-001 | .1763-001 |
| ETH | .7358-002 | .7278-002 | .1054-001 |
| OLE | .1102-001 | .1090-001 | .1578-001 |
| PAR | .2199-001 | .2175-001 | .3149-001 |
| FORM | .1701-001 | .1683-001 | .2436-001 |
| ALD | .5652-002 | .5590-002 | .8092-002 |
| ARO | .4169-002 | .4123-002 | .5969-002 |
| TOL | .2770-002 | .2740-002 | .3966-002 |
| O3 | .1382+000 | .1439+000 | .1139+000 |

AIR QUALITY AND EMISSIONS ST. LOUIS 76275

OBSERVED CONCENTRATIONS:

| SPECIES | CONCENTRATIONS (PPM) DURING SPECIFIED HOURS (L.S.T.) 5- 6 | 6- 7 | 7- 8 | 8- 9 | 9-10 | 10-11 | 11-12 | 12-13 | 13-14 | 14-15 |
|---|---|---|---|---|---|---|---|---|---|---|
| CO | .1771+001 | .3305+001 | .4013+001 | .3468+001 | .2699+001 | .2299+001 | .2122+001 | .1487+001 | .1365+001 | .1388+001 |
| NO | .1296+000 | .1872+000 | .1678+000 | .1055+000 | .3489-001 | .1420-001 | .6510-002 | .2960-002 | .2980-002 | .2730-002 |
| NO2 | .3824-001 | .4084-001 | .5692-001 | .8629-001 | .1023+000 | .9985-001 | .8254-001 | .5818-001 | .5340-001 | .5142-001 |
| NMHC | .1202+001 | .1359+001 | .1488+001 | .1209+001 | .9929+000 | .9559+000 | .9620+000 | .5959+000 | .4873+000 | .5308+000 |
| NONR | .5288-001 | .5978-001 | .6545-001 | .5320-001 | .4369-001 | .4206-001 | .4233-001 | .2622-001 | .2144-001 | .2336-001 |
| ETH | .3161-001 | .3573-001 | .3912-001 | .3180-001 | .2611-001 | .2514-001 | .2530-001 | .1567-001 | .1281-001 | .1396-001 |
| OLE | .4735-001 | .5353-001 | .5861-001 | .4764-001 | .3912-001 | .3766-001 | .3790-001 | .2348-001 | .1920-001 | .2092-001 |
| PAR | .9446-001 | .1068+000 | .1169+000 | .9504-001 | .7804-001 | .7513-001 | .7561-001 | .4684-001 | .3830-001 | .4172-001 |
| FORM | .7307-001 | .8260-001 | .9044-001 | .7352-001 | .6037-001 | .5812-001 | .5849-001 | .3623-001 | .2963-001 | .3228-001 |
| ALD | .2427-001 | .2744-001 | .3005-001 | .2443-001 | .2006-001 | .1931-001 | .1943-001 | .1204-001 | .9843-002 | .1072-001 |
| ARO | .1791-001 | .2024-001 | .2216-001 | .1802-001 | .1479-001 | .1424-001 | .1433-001 | .8879-002 | .7260-002 | .7910-002 |
| TOL | .1190-001 | .1345-001 | .1473-001 | .1197-001 | .9830-002 | .9464-002 | .9524-002 | .5900-002 | .4824-002 | .5255-002 |
| O3 | .2500-002 | .2500-002 | .2710-002 | .7010-002 | .3225-001 | .6871-001 | .1030+000 | .1346+000 | .1585+000 | .1832+000 |

| SPECIES | 15-16 | 16-17 | 17-18 |
|---|---|---|---|
| CO | .1404+001 | .1625+001 | .2922+001 |
| NO | .2760-002 | .3800-002 | .2440-001 |
| NO2 | .5671-001 | .6103-001 | .1077+000 |
| NMHC | .5354+000 | .5842+000 | .1038+001 |
| NONR | .2356-001 | .2570-001 | .4569-001 |
| ETH | .1408-001 | .1536-001 | .2731-001 |
| OLE | .2109-001 | .2302-001 | .4091-001 |
| PAR | .4208-001 | .4591-001 | .8162-001 |
| FORM | .3255-001 | .3552-001 | .6313-001 |
| ALD | .1081-001 | .1180-001 | .2098-001 |
| ARO | .7977-002 | .8704-002 | .1547-001 |
| TOL | .5300-002 | .5783-002 | .1028-001 |
| O3 | .1808+000 | .1610+000 | .8373-001 |

AIR QUALITY AND EMISSIONS ST. LOUIS 76275

INPUT AREA AND LINE SOURCE EMISSIONS:

| SPECIES | EMISSION RATES (PPM-M / MIN) DURING SPECIFIED HOURS (L.S.T.) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 5- 6 | 6- 7 | 7- 8 | 8- 9 | 9-10 | 10-11 | 11-12 | 12-13 | 13-14 | 14-15 |
| CO | .1519+001 | .2631+001 | .2388+001 | .1382+001 | .1358+001 | .1455+001 | .1512+001 | .1472+001 | .1591+001 | .1824+001 |
| NOX | .1091+000 | .1599+000 | .1611+000 | .1379+000 | .1342+000 | .1393+000 | .1432+000 | .1404+000 | .1487+000 | .1650+000 |
| THC | .7112+000 | .1007+001 | .1082+001 | .8568+000 | .8493+000 | .8785+000 | .8950+000 | .8839+000 | .9186+000 | .9983+000 |
| HC0 | .5939-001 | .8824-001 | .7976-001 | .5675-001 | .5499-001 | .5708-001 | .5874-001 | .5761-001 | .6101-001 | .6784-001 |
| HC1 | .3953-001 | .6351-001 | .5532-001 | .3714-001 | .3651-001 | .3890-001 | .4029-001 | .3936-001 | .4222-001 | .4808-001 |
| HC2 | .5371-001 | .7721-001 | .8255-001 | .6470-001 | .6441-001 | .6689-001 | .6820-001 | .6732-001 | .7010-001 | .7680-001 |
| HC3 | .1424-001 | .1989-001 | .1955-001 | .1523-001 | .1504-001 | .1558-001 | .1591-001 | .1569-001 | .1637-001 | .1771-001 |
| HC4 | .1615-001 | .2287-001 | .2667-001 | .2166-001 | .2150-001 | .2218-001 | .2255-001 | .2230-001 | .2308-001 | .2493-001 |

| | 15-16 | 16-17 | 17-18 |
|---|---|---|---|
| CO | .2254+001 | .2109+001 | .1325+001 |
| NOX | .1642+000 | .1566+000 | .8353-001 |
| THC | .1094+001 | .6222+000 | .4658+000 |
| HC0 | .7749-001 | .5758-001 | .4218-001 |
| HC1 | .5613-001 | .4674-001 | .3320-001 |
| HC2 | .8421-001 | .4748-001 | .3652-001 |
| HC3 | .1962-001 | .1307-001 | .9289-002 |
| HC4 | .2714-001 | .1421-001 | .1071-001 |

AIR QUALITY AND EMISSIONS  ST. LOUIS  76275

INPUT POINT SOURCE EMISSIONS:

| SPECIES | EMISSION RATES (PPM-M / MIN) DURING SPECIFIED HOURS (L.S.T.) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 5- 6 | 6- 7 | 7- 8 | 8- 9 | 9-10 | 10-11 | 11-12 | 12-13 | 13-14 | 14-15 |
| CO | .2881+000 | .2883+000 | .2887+000 | .2890+000 | .2891+000 | .2887+000 | .2886+000 | .2887+000 | .2890+000 | .2890+000 |
| NOX | .3030-001 | .3321-001 | .3702-001 | .4035-001 | .4088-001 | .3734-001 | .3646-001 | .3788-001 | .4032-001 | .4050-001 |
| THC | .1385+000 | .1386+000 | .2450+000 | .2452+000 | .2452+000 | .2450+000 | .2449+000 | .2450+000 | .2452+000 | .2452+000 |
| HC0 | .8115-002 | .8187-002 | .1081-001 | .1090-001 | .1093-001 | .1081-001 | .1079-001 | .1083-001 | .1091-001 | .1090-001 |
| HC1 | .2281-002 | .2284-002 | .2459-002 | .2462-002 | .2463-002 | .2459-002 | .2459-002 | .2460-002 | .2463-002 | .2462-002 |
| HC2 | .8304-002 | .8306-002 | .1684-001 | .1684-001 | .1684-001 | .1684-001 | .1684-001 | .1684-001 | .1684-001 | .1684-001 |
| HC3 | .3382-004 | .3621-004 | .3960-004 | .4277-004 | .4355-004 | .3978-004 | .3900-004 | .4035-004 | .4291-004 | .4285-004 |
| HC4 | .6805-002 | .6806-002 | .1203-001 | .1203-001 | .1203-001 | .1203-001 | .1202-001 | .1203-001 | .1203-001 | .1203-001 |

| SPECIES | 15-16 | 16-17 | 17-18 |
|---|---|---|---|
| CO | .2887+000 | .2887+000 | .2887+000 |
| NOX | .3756-001 | .3770-001 | .3789-001 |
| THC | .2450+000 | .2434+000 | .2434+000 |
| HC0 | .1082-001 | .1080-001 | .1081-001 |
| HC1 | .2460-002 | .2460-002 | .2460-002 |
| HC2 | .1684-001 | .1666-001 | .1666-001 |
| HC3 | .4018-004 | .4020-004 | .4041-004 |
| HC4 | .1203-001 | .1200-001 | .1200-001 |

AIR QUALITY AND EMISSIONS  ST. LOUIS  76275

TOTAL EMISSIONS OUTPUT:

| SPECIES | EMISSION RATES (PPM-M / MIN) DURING SPECIFIED HOURS (L.S.T.) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 5- 6 | 6- 7 | 7- 8 | 8- 9 | 9-10 | 10-11 | 11-12 | 12-13 | 13-14 | 14-15 |
| CO | .1807+001 | .2920+001 | .2677+001 | .1671+001 | .1647+001 | .1743+001 | .1801+001 | .1761+001 | .1880+001 | .2113+001 |
| NO | .1255+000 | .1738+000 | .1783+000 | .1604+000 | .1576+000 | .1590+000 | .1617+000 | .1605+000 | .1701+000 | .1850+000 |
| NO2 | .1394-001 | .1931-001 | .1981-001 | .1782-001 | .1751-001 | .1766-001 | .1797-001 | .1783-001 | .1890-001 | .2055-001 |
| NMHC | .8414+000 | .1137+001 | .1312+001 | .1087+001 | .1080+001 | .1109+001 | .1125+001 | .1114+001 | .1149+001 | .1229+001 |
| NONR | .6751-001 | .9643-001 | .9057-001 | .6765-001 | .6591-001 | .6789-001 | .6953-001 | .6844-001 | .7191-001 | .7874-001 |
| ETH | .1581-001 | .2540-001 | .2213-001 | .1485-001 | .1460-001 | .1556-001 | .1612-001 | .1575-001 | .1689-001 | .1923-001 |
| OLE | .2600-001 | .4039-001 | .3565-001 | .2474-001 | .2437-001 | .2580-001 | .2663-001 | .2608-001 | .2780-001 | .3131-001 |
| PAR | .6201-001 | .8551-001 | .9939-001 | .8154-001 | .8125-001 | .8373-001 | .8504-001 | .8416-001 | .8694-001 | .9364-001 |
| FORM | .1071-001 | .1495-001 | .1469-001 | .1146-001 | .1132-001 | .1172-001 | .1197-001 | .1180-001 | .1231-001 | .1332-001 |
| ALD | .3566-002 | .4980-002 | .4895-002 | .3816-002 | .3770-002 | .3904-002 | .3986-002 | .3931-002 | .4100-002 | .4437-002 |
| ARO | .1309-001 | .1713-001 | .2201-001 | .1901-001 | .1891-001 | .1932-001 | .1954-001 | .1940-001 | .1986-001 | .2097-001 |
| TOL | .9863-002 | .1255-001 | .1668-001 | .1468-001 | .1461-001 | .1489-001 | .1503-001 | .1493-001 | .1524-001 | .1598-001 |

| | 15-16 | 16-17 | 17-18 |
|---|---|---|---|
| CO | .2543+001 | .2397+001 | .1614+001 |
| NO | .1816+000 | .1748+000 | .1093+000 |
| NO2 | .2018-001 | .1943-001 | .1214-001 |
| NMHC | .1325+001 | .8510+000 | .6946+000 |
| NONR | .8831-001 | .6838-001 | .5299-001 |
| ETH | .2245-001 | .1869-001 | .1328-001 |
| OLE | .3614-001 | .3050-001 | .2238-001 |
| PAR | .1010+000 | .6413-001 | .5318-001 |
| FORM | .1475-001 | .9836-002 | .6999-002 |
| ALD | .4914-002 | .3276-002 | .2330-002 |
| ARO | .2229-001 | .1453-001 | .1243-001 |
| TOL | .1687-001 | .1169-001 | .1029-001 |



PBMAQE OUTPUT

AIR QUALITY AND EMISSIONS  ST. LOUIS  76275

SPECIES TO BE PLOTTED BY PBM:

CO
NO
NO2
O3
HO

INPUT DATA - PBM EXAMPLE PROBLEM

```
PBM - DAY 76275 - 10/01/76
    0    1    1    0    0    0    0    1    0    1
         20.0
        1.58       1.68       1.51        .86        .39        .39        .80        .09
         .48        .71        .79        .89        .90
       11.10      11.60      14.50      17.80      20.80      23.50      25.50      26.90
       27.80      28.50      28.70      28.20      26.10
 500.          100.00 .0000      .0000      .0000      .0000      .0000      .0000
                      .0000      .0000      .0000      .0000      .0000
 510.          100.00 .0000      .0000      .0000      .0000      .0000      .0000
                      .0000      .0000      .0000      .0000      .0000
 520.          100.00 .0000      .0000      .0000      .0000      .0000      .0000
                      .0000      .0000      .0000      .0000      .0000
 530.          100.00 .0000      .0000      .0000      .0000      .0000      .0000
                      .0000      .0000      .0000      .0000      .0000
 540.          100.00 .0000      .0000      .0000      .0000      .0000      .0000
                      .0000      .0000      .0000      .0000      .0000
 550.          100.00 .0000      .0000      .0000      .0000      .0000      .0000
                      .0000      .0000      .0000      .0000      .0000
 600.          100.00 .0000      .0000      .0000      .0000      .0000      .0000
                      .0000      .0000      .0000      .0000      .0000
 610.          100.00 .1610-002  .0000      .5685-003  .8500-005  .5892-005  .0000
                      .0000      .6439-005  .6439-005  .1529-004  .1529-004
 620.          100.29 .1089-001  .2170-005  .2094-002  .4862-005  .3343-004  .1151-004
                      .1606-005  .4358-004  .4358-004  .1035-003  .1035-003
 630.          101.24 .2432-001  .6009-005  .4505-002  .5751-005  .7391-004  .2828-004
                      .4215-005  .9727-004  .9727-004  .2310-003  .2310-003
 640.          102.96 .4118-001  .1182-004  .7544-002  .7646-005  .1257-003  .5043-004
                      .7759-005  .1647-003  .1647-003  .3912-003  .3912-003
 650.          105.54 .5762-001  .1971-004  .1053-001  .1131-004  .1785-003  .7445-004
                      .1181-004  .2305-003  .2305-003  .5474-003  .5474-003
 700.          109.11 .7652-001  .3172-004  .1401-001  .1870-004  .2422-003  .1051-003
                      .1722-004  .3061-003  .3061-003  .7269-003  .7269-003
 710.          113.77 .9557-001  .4800-004  .1760-001  .3031-004  .3108-003  .1403-003
                      .2374-004  .3823-003  .3823-003  .9079-003  .9079-003
 720.          119.64 .1158+000  .6957-004  .2145-001  .4571-004  .3875-003  .1814-003
                      .3163-004  .4631-003  .4631-003  .1100-002  .1100-002
 730.          126.85 .1345+000  .9537-004  .2509-001  .6244-004  .4634-003  .2244-003
                      .4019-004  .5381-003  .5381-003  .1278-002  .1278-002
 740.          135.50 .1526+000  .1262-003  .2864-001  .7939-004  .5406-003  .2700-003
                      .4956-004  .6105-003  .6105-003  .1450-002  .1450-002
 750.          145.74 .1714+000  .1640-003  .3234-001  .9622-004  .6239-003  .3207-003
                      .6025-004  .6856-003  .6856-003  .1628-002  .1628-002
 800.          157.56 .1920+000  .2109-003  .3642-001  .1133-003  .7179-003  .3793-003
                      .7281-004  .7679-003  .7679-003  .1824-002  .1824-002
 810.          170.80 .2131+000  .2661-003  .4064-001  .1303-003  .8182-003  .4434-003
                      .8680-004  .8526-003  .8526-003  .2025-002  .2025-002
 820.          185.25 .2335+000  .3280-003  .4472-001  .1469-003  .9184-003  .5096-003
                      .1015-003  .9338-003  .9338-003  .2218-002  .2218-002
 830.          200.69 .2502+000  .3915-003  .4812-001  .1617-003  .1007-002  .5708-003
                      .1156-003  .1001-002  .1001-002  .2377-002  .2377-002
 840.          216.92 .2669+000  .4609-003  .5153-001  .1771-003  .1096-002  .6341-003
                      .1303-003  .1067-002  .1067-002  .2535-002  .2535-002
 850.          233.73 .2831+000  .5348-003  .5485-001  .1927-003  .1185-002  .6977-003
                      .1452-003  .1132-002  .1132-002  .2689-002  .2689-002
 900.          250.91 .3010+000  .6172-003  .5851-001  .2101-003  .1281-002  .7669-003
```

INPUT DATA - PBM EXAMPLE PROBLEM

```
 57                                .1615-003 .1204-002 .1204-002 .2859-002 .2859-002
 58       910.        268.26 .3168+000 .7000-003 .6176-001 .2263-003 .1368-002 .8318-003
 59                                .1770-003 .1267-002 .1267-002 .3010-002 .3010-002
 60       920.        285.57 .3331+000 .7879-003 .6510-001 .2432-003 .1458-002 .8988-003
 61                                .1932-003 .1332-002 .1332-002 .3164-002 .3164-002
 62       930.        302.64 .3471+000 .8738-003 .6801-001 .2587-003 .1538-002 .9604-003
 63                                .2083-003 .1388-002 .1388-002 .3298-002 .3298-002
 64       940.        319.24 .3613+000 .9624-003 .7093-001 .2742-003 .1619-002 .1022-002
 65                                .2236-003 .1445-002 .1445-002 .3432-002 .3432-002
 66       950.        335.19 .3713+000 .1041-002 .7303-001 .2864-003 .1681-002 .1072-002
 67                                .2363-003 .1485-002 .1485-002 .3527-002 .3527-002
 68      1000.        350.26 .3838+000 .1128-002 .7561-001 .3005-003 .1754-002 .1129-002
 69                                .2506-003 .1535-002 .1535-002 .3646-002 .3646-002
 70      1010.        364.30 .3962+000 .1214-002 .7815-001 .3143-003 .1825-002 .1185-002
 71                                .2647-003 .1585-002 .1585-002 .3764-002 .3764-002
 72      1020.        377.32 .4059+000 .1293-002 .8015-001 .3260-003 .1885-002 .1232-002
 73                                .2770-003 .1624-002 .1624-002 .3856-002 .3856-002
 74      1030.        389.41 .4160+000 .1371-002 .8224-001 .3377-003 .1945-002 .1280-002
 75                                .2893-003 .1664-002 .1664-002 .3952-002 .3952-002
 76      1040.        400.63 .4209+000 .1428-002 .8327-001 .3449-003 .1979-002 .1310-002
 77                                .2975-003 .1684-002 .1684-002 .3998-002 .3998-002
 78      1050.        411.06 .4288+000 .1492-002 .8491-001 .3542-003 .2027-002 .1348-002
 79                                .3073-003 .1715-002 .1715-002 .4074-002 .4074-002
 80      1100.        420.77 .4328+000 .1538-002 .8576-001 .3599-003 .2054-002 .1372-002
 81                                .3138-003 .1731-002 .1731-002 .4112-002 .4112-002
 82      1110.        429.84 .4384+000 .1585-002 .8690-001 .3665-003 .2088-002 .1399-002
 83                                .3208-003 .1754-002 .1754-002 .4165-002 .4165-002
 84      1120.        438.33 .4409+000 .1615-002 .8744-001 .3702-003 .2105-002 .1414-002
 85                                .3250-003 .1764-002 .1764-002 .4188-002 .4188-002
 86      1130.        446.32 .4428+000 .1638-002 .8784-001 .3730-003 .2119-002 .1426-002
 87                                .3281-003 .1771-002 .1771-002 .4206-002 .4206-002
 88      1140.        453.88 .4441+000 .1652-002 .8812-001 .3748-003 .2127-002 .1433-002
 89                                .3302-003 .1776-002 .1776-002 .4219-002 .4219-002
 90      1150.        461.09 .4448+000 .1658-002 .8827-001 .3757-003 .2132-002 .1437-002
 91                                .3311-003 .1779-002 .1779-002 .4226-002 .4226-002
 92      1200.        468.02 .4450+000 .1656-002 .8831-001 .3757-003 .2133-002 .1437-002
 93                                .3310-003 .1780-002 .1780-002 .4227-002 .4227-002
 94      1210.        474.72 .4407+000 .1632-002 .8746-001 .3716-003 .2111-002 .1421-002
 95                                .3270-003 .1763-002 .1763-002 .4187-002 .4187-002
 96      1220.        481.17 .4376+000 .1606-002 .8682-001 .3681-003 .2092-002 .1406-002
 97                                .3232-003 .1750-002 .1750-002 .4157-002 .4157-002
 98      1230.        487.37 .4374+000 .1586-002 .8676-001 .3665-003 .2087-002 .1399-002
 99                                .3209-003 .1750-002 .1750-002 .4155-002 .4155-002
100      1240.        493.28 .4394+000 .1567-002 .8712-001 .3664-003 .2090-002 .1397-002
101                               .3196-003 .1758-002 .1758-002 .4174-002 .4174-002
102      1250.        498.89 .4372+000 .1528-002 .8665-001 .3624-003 .2072-002 .1380-002
103                               .3146-003 .1749-002 .1749-002 .4153-002 .4153-002
104      1300.        504.18 .4320+000 .1474-002 .8557-001 .3554-003 .2038-002 .1351-002
105                               .3069-003 .1728-002 .1728-002 .4104-002 .4104-002
106      1310.        509.12 .4244+000 .1407-002 .8401-001 .3462-003 .1992-002 .1313-002
107                               .2970-003 .1698-002 .1698-002 .4032-002 .4032-002
108      1320.        513.69 .4140+000 .1329-002 .8187-001 .3344-003 .1931-002 .1265-002
109                               .2847-003 .1656-002 .1656-002 .3933-002 .3933-002
110      1330.        517.88 .4039+000 .1249-002 .7979-001 .3225-003 .1871-002 .1217-002
111                               .2723-003 .1615-002 .1615-002 .3837-002 .3837-002
112      1340.        521.66 .3917+000 .1162-002 .7730-001 .3088-003 .1800-002 .1162-002
113                               .2582-003 .1567-002 .1567-002 .3721-002 .3721-002
```

INPUT DATA - PBM EXAMPLE PROBLEM

```
114      1350.          525.02 .3812+000 .1079-002 .7511-001 .2962-003 .1736-002 .1111-002
115                             .2450-003 .1525-002 .1525-002 .3621-002 .3621-002
116      1400.          527.92 .3677+000 .9888-003 .7233-001 .2811-003 .1658-002 .1050-002
117                             .2299-003 .1471-002 .1471-002 .3493-002 .3493-002
118      1410.          530.35 .3517+000 .8935-003 .6905-001 .2641-003 .1569-002 .9824-003
119                             .2132-003 .1407-002 .1407-002 .3341-002 .3341-002
120      1420.          532.00 .3383+000 .8073-003 .6628-001 .2491-003 .1491-002 .9217-003
121                             .1982-003 .1353-002 .1353-002 .3214-002 .3214-002
122      1430.          532.00 .3203+000 .7132-003 .6257-001 .2307-003 .1393-002 .8486-003
123                             .1806-003 .1281-002 .1281-002 .3042-002 .3042-002
124      1440.          532.00 .3059+000 .6315-003 .5960-001 .2152-003 .1310-002 .7860-003
125                             .1654-003 .1224-002 .1224-002 .2906-002 .2906-002
126      1450.          532.00 .2900+000 .5508-003 .5631-001 .1988-003 .1222-002 .7201-003
127                             .1498-003 .1160-002 .1160-002 .2755-002 .2755-002
128      1500.          532.00 .2770+000 .4801-003 .5360-001 .1847-003 .1145-002 .6623-003
129                             .1359-003 .1108-002 .1108-002 .2631-002 .2631-002
130      1510.          532.00 .2604+000 .4080-003 .5019-001 .1685-003 .1054-002 .5970-003
131                             .1207-003 .1041-002 .1041-002 .2474-002 .2474-002
132      1520.          532.00 .2430+000 .3408-003 .4664-001 .1521-003 .9605-003 .5322-003
133                             .1059-003 .9720-003 .9720-003 .2309-002 .2309-002
134      1530.          532.00 .2259+000 .2804-003 .4314-001 .1364-003 .8701-003 .4706-003
135                             .9193-004 .9035-003 .9035-003 .2146-002 .2146-002
136      1540.          532.00 .2056+000 .2234-003 .3906-001 .1192-003 .7702-003 .4058-003
137                             .7771-004 .8224-003 .8224-003 .1953-002 .1953-002
138      1550.          532.00 .1849+000 .1739-003 .3491-001 .1023-003 .6722-003 .3444-003
139                             .6452-004 .7394-003 .7394-003 .1756-002 .1756-002
140      1600.          532.00 .1653+000 .1333-003 .3100-001 .8660-004 .5825-003 .2896-003
141                             .5301-004 .6613-003 .6613-003 .1571-002 .1571-002
142      1610.          532.00 .1477+000 .1011-003 .2747-001 .7245-004 .5033-003 .2422-003
143                             .4324-004 .5908-003 .5908-003 .1403-002 .1403-002
144      1620.          532.00 .1280+000 .7324-004 .2359-001 .5808-004 .4207-003 .1954-003
145                             .3392-004 .5118-003 .5118-003 .1216-002 .1216-002
146      1630.          532.00 .1105+000 .5205-004 .2018-001 .4598-004 .3503-003 .1564-003
147                             .2632-004 .4419-003 .4419-003 .1050-002 .1050-002
148      1640.          525.31 .9269-001 .3556-004 .1681-001 .3542-004 .2844-003 .1219-003
149                             .1983-004 .3708-003 .3708-003 .8806-003 .8806-003
150      1650.          494.34 .7192-001 .2266-004 .1301-001 .2557-004 .2157-003 .8879-004
151                             .1398-004 .2877-003 .2877-003 .6833-003 .6833-003
152      1700.          463.38 .5116-001 .1361-004 .9284-002 .1755-004 .1517-003 .6007-004
153                             .9173-005 .2046-003 .2046-003 .4860-003 .4860-003
154      1710.          432.42 .3140-001 .7347-005 .5787-002 .1118-004 .9362-004 .3533-004
155                             .5225-005 .1256-003 .1256-003 .2983-003 .2983-003
156      1720.          401.45 .1448-001 .2745-005 .2819-002 .6515-005 .4480-004 .1484-004
157                             .2019-005 .5791-004 .5791-004 .1375-003 .1375-003
158      1730.          370.49 .0000     .0000     .0000     .0000     .0000     .0000
159                             .0000     .0000     .0000     .0000     .0000
160      1740.          339.53 .0000     .0000     .0000     .0000     .0000     .0000
161                             .0000     .0000     .0000     .0000     .0000
162      1750.          314.60 .0000     .0000     .0000     .0000     .0000     .0000
163                             .0000     .0000     .0000     .0000     .0000
164      1800.          308.78 .0000     .0000     .0000     .0000     .0000     .0000
165                             .0000     .0000     .0000     .0000     .0000
166       500.           -1.00 .0000     .0000     .0000     .0000     .0000     .0000
167                             .0000     .0000     .0000     .0000     .0000
168         14       INITIAL CONCENTRATIONS
169       CO         .1622+001
170       NO         .1239+000
```

```
INPUT DATA - PBM EXAMPLE PROBLEM

   171      NO2          .3910-001
   172      NMHC         .1199+001
   173      NONR         .5276-001
   174      ETH          .3154-001
   175      OLE          .4724-001
   176      PAR          .9425-001
   177      FORM         .7291-001
   178      ALD          .2422-001
   179      ARO          .1787-001
   180      TOL          .1187-001
   181      O3           .2500-002
   182      H2O          .7879+004
   183          1        TOP BOUNDARY CONCENTRATIONS
   184      O3           .6300-001 .6300-001 .6300-001 .6300-001 .6300-001 .6300-001 .6300-001
   185                   .6300-001 .6300-001 .6300-001 .6300-001 .6300-001 .6300-001
   186         13 LATERAL BOUNDARY CONCENTRATIONS
   187      CO           .6648+000 .9467+000 .8884+000 .8027+000 .8145+000 .8069+000 .6851-001
   188                   .2796+000 .3172+000 .4243+000 .3888+000 .5457+000 .8985+000
   189      NO           .4121-001 .3570-001 .3076-001 .1685-001 .1240-001 .4890-002 .2500-002
   190                   .2500-002 .2500-002 .2500-002 .2550-002 .2610-002 .2980-002
   191      NO2          .1933-001 .2250-001 .2729-001 .4307-001 .4161-001 .2248-001 .9790-002
   192                   .7830-002 .9360-002 .3420-002 .2562-001 .2373-001 .3179-001
   193      NMHC         .6050+000 .5300+000 .3006+000 .2977+000 .2806+000 .2806+000 .2180+000
   194                   .1550+000 .1470+000 .1787+000 .2798+000 .2767+000 .4006+000
   195      NONR         .2662-001 .2332-001 .1323-001 .1310-001 .1235-001 .1235-001 .9592-002
   196                   .6820-002 .6468-002 .7865-002 .1231-001 .1218-001 .1763-001
   197      ETH          .1591-001 .1394-001 .7906-002 .7830-002 .7381-002 .7381-002 .5733-002
   198                   .4076-002 .3866-002 .4701-002 .7358-002 .7278-002 .1054-001
   199      OLE          .2384-001 .2088-001 .1184-001 .1173-001 .1106-001 .1106-001 .8589-002
   200                   .6107-002 .5792-002 .7042-002 .1102-001 .1090-001 .1578-001
   201      PAR          .4755-001 .4166-001 .2363-001 .2340-001 .2206-001 .2206-001 .1713-001
   202                   .1218-001 .1155-001 .1405-001 .2199-001 .2175-001 .3149-001
   203      FORM         .3678-001 .3222-001 .1828-001 .1810-001 .1706-001 .1706-001 .1325-001
   204                   .9424-002 .8938-002 .1087-001 .1701-001 .1683-001 .2436-001
   205      ALD          .1222-001 .1071-001 .6072-002 .6014-002 .5669-002 .5669-002 .4404-002
   206                   .3131-002 .2969-002 .3611-002 .5652-002 .5590-002 .8092-002
   207      ARO          .9014-002 .7897-002 .4479-002 .4436-002 .4181-002 .4181-002 .3248-002
   208                   .2309-002 .2190-002 .2663-002 .4169-002 .4123-002 .5969-002
   209      TOL          .5989-002 .5247-002 .2976-002 .2947-002 .2778-002 .2778-002 .2158-002
   210                   .1534-002 .1455-002 .1770-002 .2770-002 .2740-002 .3966-002
   211      O3           .1018-001 .5050-002 .1328-001 .2404-001 .3312-001 .5421-001 .8282-001
   212                   .1015+000 .1037+000 .1286+000 .1382+000 .1439+000 .1139+000
   213         13        OBSERVED CONCENTRATIONS
   214      CO           .1771+001 .3305+001 .4013+001 .3468+001 .2699+001 .2299+001 .2122+001
   215                   .1487+001 .1365+001 .1388+001 .1404+001 .1625+001 .2922+001
   216      NO           .1296+000 .1872+000 .1678+000 .1055+000 .3489-001 .1420-001 .6510-002
   217                   .2960-002 .2980-002 .2730-002 .2760-002 .3800-002 .2440-001
   218      NO2          .3824-001 .4084-001 .5692-001 .8629-001 .1023+000 .9985-001 .8254-001
   219                   .5818-001 .5340-001 .5142-001 .5671-001 .6103-001 .1077+000
   220      NMHC         .1202+001 .1359+001 .1488+001 .1209+001 .9929+000 .9559+000 .9620+000
   221                   .5959+000 .4873+000 .5308+000 .5354+000 .5842+000 .1038+001
   222      NONR         .5288-001 .5978-001 .6545-001 .5320-001 .4369-001 .4206-001 .4233-001
   223                   .2622-001 .2144-001 .2336-001 .2356-001 .2570-001 .4569-001
   224      ETH          .3161-001 .3573-001 .3912-001 .3180-001 .2611-001 .2514-001 .2530-001
   225                   .1567-001 .1281-001 .1396-001 .1408-001 .1536-001 .2731-001
   226      OLE          .4735-001 .5353-001 .5861-001 .4764-001 .3912-001 .3766-001 .3790-001
   227                   .2348-001 .1920-001 .2092-001 .2109-001 .2302-001 .4091-001
```

```
INPUT DATA - PBM EXAMPLE PROBLEM

   228      PAR          .9446-001 .1068+000 .1169+000 .9504-001 .7804-001 .7513-001 .7561-001
   229                   .4684-001 .3830-001 .4172-001 .4208-001 .4591-001 .8162-001
   230      FORM         .7307-001 .8260-001 .9044-001 .7352-001 .6037-001 .5812-001 .5849-001
   231                   .3623-001 .2963-001 .3228-001 .3255-001 .3552-001 .6313-001
   232      ALD          .2427-001 .2744-001 .3005-001 .2443-001 .2006-001 .1931-001 .1943-001
   233                   .1204-001 .9843-002 .1072-001 .1081-001 .1180-001 .2098-001
   234      ARO          .1791-001 .2024-001 .2216-001 .1802-001 .1479-001 .1424-001 .1433-001
   235                   .8879-002 .7260-002 .7910-002 .7977-002 .8704-002 .1547-001
   236      TOL          .1190-001 .1345-001 .1473-001 .1197-001 .9830-002 .9464-002 .9524-002
   237                   .5900-002 .4824-002 .5255-002 .5300-002 .5783-002 .1028-001
   238      O3           .2500-002 .2500-002 .2710-002 .7010-002 .3225-001 .6871-001 .1030+000
   239                   .1346+000 .1585+000 .1832+000 .1808+000 .1610+000 .8373-001
   240         12        EMISSIONS SPECIES
   241      CO           .1807+001 .2920+001 .2677+001 .1671+001 .1647+001 .1743+001 .1801+001
   242                   .1761+001 .1880+001 .2113+001 .2543+001 .2397+001 .1614+001
   243      NO           .1255+000 .1738+000 .1783+000 .1604+000 .1576+000 .1590+000 .1617+000
   244                   .1605+000 .1701+000 .1850+000 .1816+000 .1748+000 .1093+000
   245      NO2          .1394-001 .1931-001 .1981-001 .1782-001 .1751-001 .1766-001 .1797-001
   246                   .1783-001 .1890-001 .2055-001 .2018-001 .1943-001 .1214-001
   247      NMHC         .8414+000 .1137+001 .1312+001 .1087+001 .1080+001 .1109+001 .1125+001
   248                   .1114+001 .1149+001 .1229+001 .1325+001 .8510+000 .6946+000
   249      NONR         .6751-001 .9643-001 .9057-001 .6765-001 .6591-001 .6789-001 .6953-001
   250                   .6844-001 .7191-001 .7874-001 .8831-001 .6838-001 .5299-001
   251      ETH          .1581-001 .2540-001 .2213-001 .1485-001 .1460-001 .1556-001 .1612-001
   252                   .1575-001 .1689-001 .1923-001 .2245-001 .1869-001 .1328-001
   253      OLE          .2600-001 .4039-001 .3565-001 .2474-001 .2437-001 .2580-001 .2663-001
   254                   .2608-001 .2780-001 .3131-001 .3614-001 .3050-001 .2238-001
   255      PAR          .6201-001 .8551-001 .9939-001 .8154-001 .8125-001 .8373-001 .8504-001
   256                   .8416-001 .8694-001 .9364-001 .1010+000 .6413-001 .5318-001
   257      FORM         .1071-001 .1495-001 .1469-001 .1146-001 .1132-001 .1172-001 .1197-001
   258                   .1180-001 .1231-001 .1332-001 .1475-001 .9836-002 .6999-002
   259      ALD          .3566-002 .4980-002 .4895-002 .3816-002 .3770-002 .3904-002 .3986-002
   260                   .3931-002 .4100-002 .4437-002 .4914-002 .3276-002 .2330-002
   261      ARO          .1309-001 .1713-001 .2201-001 .1901-001 .1891-001 .1932-001 .1954-001
   262                   .1940-001 .1986-001 .2097-001 .2229-001 .1453-001 .1243-001
   263      TOL          .9863-002 .1255-001 .1668-001 .1468-001 .1461-001 .1489-001 .1503-001
   264                   .1493-001 .1524-001 .1598-001 .1687-001 .1169-001 .1029-001
   265           5       PLOT SPECIES
   266      CO
   267      NO
   268      NO2
   269      O3
   270      HO
**
```

```
PBM - DAY 76275 - 10/01/76

TOTAL NUMBER OF REACTIONS =  63
NUMBER OF REACTIVE SPECIES =  37
NUMBER OF INERT OR CONSTANT SPECIES =   4
NUMBER OF SPECIES WITH TOP BOUNDARY CONDITIONS =   1
NUMBER OF SPECIES WITH SIDE BOUNDARY CONDITIONS =  13
NUMBER OF SPECIES WITH SOURCE EMISSIONS TERMS =  12
NUMBER OF SPECIES WITH OBSERVED CONCENTRATIONS =  13
NUMBER OF SPECIES TO BE PLOTTED =   5
NUMBER OF PHOTOLYZING SPECIES =  11
PHOTOLYSIS REACTION NUMBERS =      1     5    12    25    32    33    37    52    53    55    56
HOURS OF SIMULATION INPUT DATA TO BE READ =  13
ENDING TIME OF SIMULATION IN MINUTES FROM START =  780.00
STARTING TIME OF SIMULATION =  0500 L.S.T.
TIME INTERVAL FOR PRINTING/PLOTTING CONCENTRATIONS (MINUTES) =   10.00
TIME INTERVAL FOR UPDATING PHOTOLYTIC RATE CONSTANTS AND MIXING HEIGHTS (MINUTES) =   10.00
NUMERICAL CONVERGENCE TOLERANCE =   .0100
WIDTH OF SIMULATED BOX AREA (METERS) =   20000.00
HOURLY AMBIENT TEMPERATURES ARE SPECIFIED
```

SPECIES CONTROL INFORMATION

| SPECIE | TOP B.C. | SIDE B.C. | SOURCE EMISSIONS | OBS. CONC. | PLOT |
|---|---|---|---|---|---|
| CO | | * | * | * | * |
| NO | | * | * | * | * |
| NO2 | | * | * | * | * |
| NMHC | | * | * | * | |
| NONR | | * | * | * | |
| ETH | | * | * | * | |
| OLE | | * | * | * | |
| PAR | | * | * | * | |
| FORM | | * | * | * | |
| ALD | | * | * | * | |
| ARO | | * | * | * | |
| TOL | | * | * | * | |
| O3 | * | * | | * | * |
| HONO | | | | | |
| HNO3 | | | | | |
| PAN | | | | | |
| DCB1 | | | | | |
| DCB2 | | | | | |
| RNO3 | | | | | |
| H2O2 | | | | | |
| O | | | | | |
| O1D | | | | | |
| NO3 | | | | | |
| N2O5 | | | | | |
| HO | | | | | * |
| HO2 | | | | | |
| HO4N | | | | | |
| RO | | | | | |
| RO2 | | | | | |
| RTO | | | | | |
| RXO | | | | | |
| FRO2 | | | | | |
| FRO | | | | | |
| R1O2 | | | | | |
| RTO2 | | | | | |
| RXO2 | | | | | |
| COOH | | | | | |
| O2 | | | | | |
| CO2 | | | | | |
| M | | | | | |
| H2O | | | | | |

LIST OF REACTIONS

| | R. CONST. * | REACTANTS | | | | PRODUCTS | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | .0000 | | | NO2 | = | 1.00 | NO | 1.00 | O | | |
| 2 | .0000 | O | O2 | M | = | 1.00 | O3 | 1.00 | M | | |
| 3 | .0000 | | O3 | NO | = | 1.00 | NO2 | 1.00 | O2 | | |
| 4 | .0000 | | O3 | NO2 | = | 1.00 | NO3 | 1.00 | O2 | | |
| 5 | .0000 | | | O3 | = | 1.00 | O1D | 1.00 | O2 | | |
| 6 | .0000 | | O1D | M | = | 1.00 | O | 1.00 | M | | |
| 7 | .3400+006 | | O1D | H2O | = | 2.00 | HO | | | | |
| 8 | .2960+005 | | NO3 | NO | = | 2.00 | NO2 | | | | |
| 9 | .1780+004 | | NO3 | NO2 | = | 1.00 | N2O5 | | | | |
| 10 | .0000 | | | N2O5 | = | 1.00 | NO3 | 1.00 | NO2 | | |
| 11 | .1920-004 | | N2O5 | H2O | = | 2.00 | HNO3 | | | | |
| 12 | .0000 | | | HONO | = | 1.00 | HO | 1.00 | NO | | |
| 13 | .4140+003 | | HO | CO | = | 1.00 | HO2 | 1.00 | CO2 | | |
| 14 | .4400+001 | | HO2 | NO2 | = | 1.00 | HONO | 1.00 | O2 | | |
| 15 | .0000 | | HO2 | NO | = | 1.00 | HO | 1.00 | NO2 | | |
| 16 | .0000 | HO2 | NO2 | M | = | 1.00 | HO4N | 1.00 | M | | |
| 17 | .0000 | | | HO4N | = | 1.00 | HO2 | 1.00 | NO2 | | |
| 18 | .9750+004 | | HO | HONO | = | 1.00 | NO2 | 1.00 | H2O | | |
| 19 | .0000 | HO | NO2 | M | = | 1.00 | HNO3 | 1.00 | M | | |
| 20 | .0000 | HO | NO | M | = | 1.00 | HONO | 1.00 | M | | |
| 21 | .0000 | | HO | HNO3 | = | 1.00 | H2O | 1.00 | NO3 | | |
| 22 | .0000 | | HO2 | O3 | = | 1.00 | HO | 2.00 | O2 | | |
| 23 | .0000 | | HO | O3 | = | 1.00 | HO2 | 1.00 | O2 | | |
| 24 | .0000 | | HO2 | HO2 | = | 1.00 | H2O2 | 1.00 | O2 | | |
| 25 | .0000 | | | H2O2 | = | 2.00 | HO | | | | |
| 26 | .2500-002 | | ETH | O3 | = | .40 | RO2 | 1.00 | FORM | .10 | HO2 |
| 27 | .1200+005 | | ETH | HO | = | 1.00 | FRO2 | 1.00 | FORM | | |
| 28 | .5100+004 | | OLE | O | = | 1.00 | RO2 | 1.00 | ALD | 1.00 | HO2 |
| 29 | .9500-001 | | OLE | O3 | = | .75 | RO2 | .75 | ALD | .40 | HO2 |
| 30 | .5500+005 | | OLE | HO | = | 1.00 | RO2 | .75 | ALD | .25 | FORM |
| 31 | .5000+004 | | PAR | HO | = | 1.00 | RO2 | | | | |
| 32 | .0000 | | | FORM | = | 1.00 | CO | | | | |
| 33 | .0000 | | | FORM | = | 2.00 | HO2 | 1.00 | CO | | |
| 34 | .1600+005 | | FORM | HO | = | 1.00 | HO2 | 1.00 | H2O | 1.00 | CO |
| 35 | .1100+005 | | RO2 | NO | = | 1.00 | RO | 1.00 | NO2 | | |
| 36 | .0000 | | RO | O2 | = | .75 | ALD | 1.00 | HO2 | .25 | FORM |
| 37 | .0000 | | | ALD | = | 1.00 | RO2 | 1.00 | HO2 | 1.00 | CO |
| 38 | .2400+005 | | ALD | HO | = | 1.00 | R1O2 | 1.00 | H2O | | |
| 39 | .1100+005 | | FRO2 | NO | = | 1.00 | FRO | 1.00 | NO2 | | |
| 40 | .1080+001 | | FRO | O2 | = | 1.00 | FORM | 1.00 | HO2 | | |
| 41 | .8870+004 | | R1O2 | NO2 | = | 1.00 | PAN | | | | |
| 42 | .0000 | | | PAN | = | 1.00 | R1O2 | 1.00 | NO2 | | |
| 43 | .1000+003 | | RO | NO2 | = | 1.00 | RNO3 | | | | |
| 44 | .2000+001 | | RO2 | O3 | = | 1.00 | RO | 2.00 | O2 | | |
| 45 | .2070+005 | | R1O2 | NO | = | 1.00 | RO2 | 1.00 | NO2 | | |
| 46 | .8700+004 | | TOL | HO | = | 1.00 | RTO2 | 1.00 | ALD | 1.00 | DCB1 |
| 47 | .3400+005 | | ARO | HO | = | 1.00 | RXO2 | 1.00 | ALD | 1.00 | DCB1 |
| 48 | .1100+005 | | RTO2 | NO | = | 1.00 | RTO | 1.00 | NO2 | | |
| 49 | .8870+000 | | RTO | O2 | = | 1.00 | DCB1 | 1.00 | HO2 | 1.00 | CO |
| 50 | .1100+005 | | RXO2 | NO | = | 1.00 | RXO | 1.00 | NO2 | | |
| 51 | .8870+000 | | RXO | O2 | = | 1.00 | DCB2 | 1.00 | HO2 | 1.00 | CO |
| 52 | .0000 | | | DCB1 | = | 2.00 | CO | 2.00 | HO2 | | |
| 53 | .0000 | | | DCB1 | = | .20 | FORM | 1.80 | CO | | |

```
54  .1700+005          DCB1 HO    =  1.00 HO2    2.00 CO
55  .0000                   DCB2  =  1.00 R102   1.00 HO2    2.00 CO
56  .0000                   DCB2  =   .50 ALD     .50 FORM    .50 FRO2
57  .2560+005          DCB2 HO    =  1.00 R102   1.00 CO
58  .2000+001          RTO2 O3    =  1.00 RTO    2.00 O2
59  .2000+001          RXO2 O3    =  1.00 RXO    2.00 O2
60  .2000+001          R102 O3    =  1.00 RO2    2.00 O2
61  .1500-002          OLE  O3    =  1.00 COOH   1.00 ALD
62  .0000                   NRHC  =
63  .0000                   NONR  =
```

* ONLY TEMPORALLY-FIXED RATE CONSTANT VALUES ARE GIVEN HERE.
  VALUES OF OTHER RATE CONSTANTS ARE SHOWN AT EACH TIME STEP.

INITIAL SPECIES CONCENTRATIONS

| SPECIES | VALUE | SPECIES | VALUE | SPECIES | VALUE | SPECIES | VALUE |
|---|---|---|---|---|---|---|---|
| REACTIVE (PPM) | | | | | | | |
| CO | .1622+001 | NO | .1239+000 | NO2 | .3910-001 | NMHC | .1199+001 |
| HCHO | .5276-001 | ETH | .3154-001 | OLE | .4724-001 | PAR | .9425-001 |
| FORM | .7291-001 | ALD | .2422-001 | ARO | .1787-001 | TOL | .1187-001 |
| O3 | .2500-002 | HONO | .0000 | HNO3 | .0000 | PAN | .0000 |
| DCB1 | .0000 | DCB2 | .0000 | RNO3 | .0000 | H2O2 | .1000-005 |
| O | .0000 | O1D | .0000 | NO3 | .0000 | N2O5 | .0000 |
| HO | .0000 | HO2 | .0000 | HO4N | .0000 | RO | .0000 |
| RO2 | .0000 | RTO | .0000 | RXO | .0000 | FRO2 | .0000 |
| FRO | .0000 | R1O2 | .0000 | RTO2 | .0000 | RXO2 | .0000 |
| COOH | .0000 | | | | | | |
| INERT/CONSTANT (PPM) | | | | | | | |
| O2 | .2100+006 | CO2 | .3200+003 | M | .1000+007 | H2O | .7879+004 |

TIME = 782.969 MINUTES

PHOTOLYTIC RATE CONSTANTS:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| RK( 1) = | .0000 | RK( 5) = | .0000 | RK(12) = | .0000 | RK(25) = | .0000 |
| RK(32) = | .0000 | RK(33) = | .0000 | RK(37) = | .0000 | RK(52) = | .0000 |
| RK(53) = | .0000 | RK(55) = | .0000 | RK(56) = | .0000 | | |

TEMPERATURE-DEPENDENT RATE CONSTANTS:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| RK( 2) = | .2231-004 | RK( 3) = | .2733+002 | RK( 4) = | .4926-001 | RK( 6) = | .4229+005 |
| RK(10) = | .3630+001 | RK(15) = | .1220+005 | RK(16) = | .1500-002 | RK(17) = | .3755+001 |
| RK(19) = | .1425-001 | RK(20) = | .7315-002 | RK(21) = | .1948+003 | RK(22) = | .2980+001 |
| RK(23) = | .1020+003 | RK(24) = | .3667+004 | RK(36) = | .9251+000 | RK(42) = | .1627+000 |

Z = 388.8 METERS WIND SPEED = 54.0 M/MIN TEMP = 299.3(K)

CONCENTRATIONS:

| SPECIES | VALUE | SPECIES | VALUE | SPECIES | VALUE | SPECIES | VALUE |
|---|---|---|---|---|---|---|---|
| CO | .1961+001 | NO | .4738-004 | NO2 | .5870-001 | NMHC | .1001+001 |
| HCHO | .6276-001 | ETH | .1367-001 | OLE | .5080-002 | PAR | .6810-001 |
| FORM | .2787-001 | ALD | .4971-001 | ARO | .9295-002 | TOL | .1040-001 |
| O3 | .1352+000 | HONO | .8345-003 | HNO3 | .8336-001 | PAN | .5363-002 |
| DCB1 | .5617-002 | DCB2 | .2221-002 | RNO3 | .2651-005 | H2O2 | .4314-003 |
| O | .7333-014 | O1D | .2191-021 | NO3 | .7410-004 | N2O5 | .2053-002 |
| HO | .1293-007 | HO2 | .6179-004 | HO4N | .1446-002 | RO | .3125-009 |
| RO2 | .7533-004 | RTO | .6189-011 | RXO | .2157-010 | FRO2 | .4037-005 |
| FRO | .9243-011 | R1O2 | .1703-005 | RTO2 | .1463-005 | RXO2 | .5101-005 |
| COOH | .2559-003 | | | | | | |

THIS SIMULATION ENDED WITH KFLAG = 1

HOUR-AVERAGE SIMULATION RESULTS FOR REACTIVE SPECIES:

HOUR-AVERAGES CENTERED AT 5.50 HRS, LOCAL STANDARD TIME

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO | .1999+001 | NO | .1444+000 | NO2 | .4392-001 | NMHC | .1355+001 |
| NONR | .6811-001 | ETH | .3388-001 | OLE | .5138-001 | PAR | .1054+000 |
| FORM | .7113-001 | ALD | .2366-001 | ARO | .2034-001 | TOL | .1384-001 |
| O3 | .1586-004 | HONO | .4377-005 | HNO3 | .2284-005 | PAN | .1804-006 |
| DCB1 | .3596-005 | DCB2 | .2692-005 | RNO3 | .4445-009 | H2O2 | .8690-006 |
| O | .0000 | O1D | .0000 | NO3 | .5220-011 | N2O5 | .5355-009 |
| HO | .5142-010 | HO2 | .2506-009 | HO4N | .3448-007 | RO | .1892-011 |
| RO2 | .1645-009 | RTO | .3297-013 | RXO | .1896-012 | FRO2 | .1327-010 |
| FRO | .9181-013 | R1O2 | .9610-011 | RTO2 | .3905-011 | RXO2 | .2247-010 |
| COOH | .9313-007 | | | | | | |

HOUR-AVERAGES CENTERED AT 6.50 HRS, LOCAL STANDARD TIME

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO | .2812+001 | NO | .1853+000 | NO2 | .4872-001 | NMHC | .1619+001 |
| NONR | .9576-001 | ETH | .3870-001 | OLE | .5943-001 | PAR | .1245+000 |
| FORM | .6763-001 | ALD | .2274-001 | ARO | .2438-001 | TOL | .1700-001 |
| O3 | .2905-003 | HONO | .4830-004 | HNO3 | .2621-004 | PAN | .1574-005 |
| DCB1 | .4012-004 | DCB2 | .2944-004 | RNO3 | .6290-008 | H2O2 | .6562-006 |
| O | .2225-009 | O1D | .8378-019 | NO3 | .8243-010 | N2O5 | .9196-008 |
| HO | .2679-008 | HO2 | .1136-007 | HO4N | .1304-005 | RO | .9801-010 |
| RO2 | .6322-008 | RTO | .2214-011 | RXO | .1234-010 | FRO2 | .6019-009 |
| FRO | .5689-011 | R1O2 | .3316-009 | RTO2 | .1924-009 | RXO2 | .1073-008 |
| COOH | .4284-006 | | | | | | |

HOUR-AVERAGES CENTERED AT 7.50 HRS, LOCAL STANDARD TIME

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO | .3099+001 | NO | .1762+000 | NO2 | .6154-001 | NMHC | .1601+001 |
| NONR | .1020+000 | ETH | .3599-001 | OLE | .5429-001 | PAR | .1222+000 |
| FORM | .5381-001 | ALD | .2145-001 | ARO | .2413-001 | TOL | .1741-001 |
| O3 | .2134-002 | HONO | .5034-003 | HNO3 | .4750-003 | PAN | .2476-004 |
| DCB1 | .5961-003 | DCB2 | .4234-003 | RNO3 | .1012-006 | H2O2 | .4102-006 |
| O | .1549-008 | O1D | .5050-017 | NO3 | .9600-009 | N2O5 | .1074-006 |
| HO | .2184-007 | HO2 | .9343-007 | HO4N | .1019-004 | RO | .6522-009 |
| RO2 | .5150-007 | RTO | .1752-010 | RXO | .9438-010 | FRO2 | .5053-008 |
| FRO | .4158-010 | R1O2 | .3127-008 | RTO2 | .1752-008 | RXO2 | .9431-008 |
| COOH | .4531-005 | | | | | | |

HOUR-AVERAGES CENTERED AT 8.50 HRS, LOCAL STANDARD TIME

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO | .2395+001 | NO | .1064+000 | NO2 | .7914-001 | NMHC | .1235+001 |
| NONR | .7856-001 | ETH | .2494-001 | OLE | .3437-001 | PAR | .9313-001 |
| FORM | .3592-001 | ALD | .2258-001 | ARO | .1805-001 | TOL | .1388-001 |
| O3 | .8195-002 | HONO | .8082-003 | HNO3 | .2284-002 | PAN | .1403-003 |
| DCB1 | .1877-002 | DCB2 | .1252-002 | RNO3 | .3669-006 | H2O2 | .2263-006 |
| O | .3864-008 | O1D | .7284-016 | NO3 | .8995-008 | N2O5 | .8983-006 |
| HO | .5892-007 | HO2 | .3172-006 | HO4N | .2958-004 | RO | .1192-008 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| RO2 | .1704-006 | RTO | .3761-010 | RXO | .1903-009 | FRO2 | .1683-007 |
| FRO | .8242-010 | R1O2 | .1566-007 | RTO2 | .6326-008 | RXO2 | .3189-007 |
| COOH | .1512-004 | | | | | | |

HOUR-AVERAGES CENTERED AT 9.50 HRS, LOCAL STANDARD TIME

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO | .1816+001 | NO | .5504-001 | NO2 | .8894-001 | NMHC | .9673+000 |
| NONR | .6064-001 | ETH | .1737-001 | OLE | .1953-001 | PAR | .7153-001 |
| FORM | .2630-001 | ALD | .2698-001 | ARO | .1293-001 | TOL | .1094-001 |
| O3 | .2276-001 | HONO | .5822-003 | HNO3 | .6103-002 | PAN | .4727-003 |
| DCB1 | .3226-002 | DCB2 | .1952-002 | RNO3 | .7385-006 | H2O2 | .1970-006 |
| O | .6211-008 | O1D | .4357-015 | NO3 | .5624-007 | N2O5 | .4465-005 |
| HO | .9346-007 | HO2 | .7615-006 | HO4N | .5465-004 | RO | .1349-008 |
| RO2 | .3929-006 | RTO | .4755-010 | RXO | .2190-009 | FRO2 | .3848-007 |
| FRO | .9921-010 | R1O2 | .5598-007 | RTO2 | .1517-007 | RXO2 | .6952-007 |
| COOH | .3451-004 | | | | | | |

HOUR-AVERAGES CENTERED AT 10.50 HRS, LOCAL STANDARD TIME

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO | .1612+001 | NO | .3137-001 | NO2 | .9235-001 | NMHC | .8745+000 |
| NONR | .5425-001 | ETH | .1406-001 | OLE | .1156-001 | PAR | .6313-001 |
| FORM | .2282-001 | ALD | .3319-001 | ARO | .1026-001 | TOL | .9733-002 |
| O3 | .4654-001 | HONO | .3640-003 | HNO3 | .1195-001 | PAN | .1048-002 |
| DCB1 | .4436-002 | DCB2 | .2385-002 | RNO3 | .1181-005 | H2O2 | .4278-006 |
| O | .7919-008 | O1D | .1385-014 | NO3 | .2188-006 | N2O5 | .1323-004 |
| HO | .1215-006 | HO2 | .1546-005 | HO4N | .8199-004 | RO | .1432-008 |
| RO2 | .7716-006 | RTO | .5515-010 | RXO | .2267-009 | FRO2 | .7446-007 |
| FRO | .1106-009 | R1O2 | .1548-006 | RTO2 | .3054-007 | RXO2 | .1250-006 |
| COOH | .6234-004 | | | | | | |

HOUR-AVERAGES CENTERED AT 11.50 HRS, LOCAL STANDARD TIME

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO | .1517+001 | NO | .1884-001 | NO2 | .9105-001 | NMHC | .8451+000 |
| NONR | .5194-001 | ETH | .1234-001 | OLE | .7069-002 | PAR | .5949-001 |
| FORM | .2161-001 | ALD | .3849-001 | ARO | .8577-002 | TOL | .9125-002 |
| O3 | .7856-001 | HONO | .2409-003 | HNO3 | .1893-001 | PAN | .1792-002 |
| DCB1 | .5316-002 | DCB2 | .2545-002 | RNO3 | .1629-005 | H2O2 | .1328-005 |
| O | .8538-008 | O1D | .2827-014 | NO3 | .6317-006 | N2O5 | .2957-004 |
| HO | .1424-006 | HO2 | .2813-005 | HO4N | .1135-003 | RO | .1476-008 |
| RO2 | .1384-005 | RTO | .6065-010 | RXO | .2226-009 | FRO2 | .1300-006 |
| FRO | .1164-009 | R1O2 | .3447-006 | RTO2 | .5572-007 | RXO2 | .2036-006 |
| COOH | .9125-004 | | | | | | |

HOUR-AVERAGES CENTERED AT 12.50 HRS, LOCAL STANDARD TIME

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO | .1511+001 | NO | .1221-001 | NO2 | .9019-001 | NMHC | .8623+000 |
| NONR | .5275-001 | ETH | .1139-001 | OLE | .4394-002 | PAR | .5908-001 |
| FORM | .2135-001 | ALD | .4350-001 | ARO | .7561-002 | TOL | .8997-002 |
| O3 | .1150+000 | HONO | .1756-003 | HNO3 | .2731-001 | PAN | .2690-002 |
| DCB1 | .6077-002 | DCB2 | .2623-002 | RNO3 | .2115-005 | H2O2 | .3961-005 |
| O | .8528-008 | O1D | .4072-014 | NO3 | .1444-005 | N2O5 | .5687-004 |
| HO | .1497-006 | HO2 | .4395-005 | HO4N | .1472-003 | RO | .1461-008 |
| RO2 | .2158-005 | RTO | .6290-010 | RXO | .2066-009 | FRO2 | .1948-006 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| FRO | .1144-009 | R1O2 | .6252-006 | RTO2 | .8800-007 | RXO2 | .2882-006 |
| COOH | .1210-003 | | | | | | |

HOUR-AVERAGES CENTERED AT 13.50 HRS, LOCAL STANDARD TIME

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO | .1579+001 | NO | .8506-002 | NO2 | .9092-001 | NMHC | .9040+000 |
| NONR | .5528-001 | ETH | .1088-001 | OLE | .3053-002 | PAR | .6043-001 |
| FORM | .2151-001 | ALD | .4766-001 | ARO | .7026-002 | TOL | .9143-002 |
| O3 | .1507+000 | HONO | .1380-003 | HNO3 | .3628-001 | PAN | .3526-002 |
| DCB1 | .6627-002 | DCB2 | .2614-002 | RNO3 | .2617-005 | H2O2 | .9144-005 |
| O | .8032-008 | O1D | .4281-014 | NO3 | .2786-005 | N2O5 | .9881-004 |
| HO | .1403-006 | HO2 | .5953-005 | HO4N | .1786-003 | RO | .1366-008 |
| RO2 | .2948-005 | RTO | .5990-010 | RXO | .1800-009 | FRO2 | .2515-006 |
| FRO | .1031-009 | R1O2 | .9209-006 | RTO2 | .1198-006 | RXO2 | .3592-006 |
| COOH | .1477-003 | | | | | | |

HOUR-AVERAGES CENTERED AT 14.50 HRS, LOCAL STANDARD TIME

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO | .1637+001 | NO | .5691-002 | NO2 | .9036-001 | NMHC | .9316+000 |
| NONR | .5696-001 | ETH | .1067-001 | OLE | .2794-002 | PAR | .6143-001 |
| FORM | .2191-001 | ALD | .4936-001 | ARO | .6860-002 | TOL | .9225-002 |
| O3 | .1768+000 | HONO | .1178-003 | HNO3 | .4298-001 | PAN | .4031-002 |
| DCB1 | .6695-002 | DCB2 | .2497-002 | RNO3 | .2922-005 | H2O2 | .1709-004 |
| O | .6461-008 | O1D | .2991-014 | NO3 | .4896-005 | N2O5 | .1589-003 |
| HO | .1163-006 | HO2 | .7472-005 | HO4N | .2041-003 | RO | .1161-008 |
| RO2 | .3797-005 | RTO | .5010-010 | RXO | .1456-009 | FRO2 | .3022-006 |
| FRO | .8290-010 | R1O2 | .1168-005 | RTO2 | .1493-006 | RXO2 | .4338-006 |
| COOH | .1682-003 | | | | | | |

HOUR-AVERAGES CENTERED AT 15.50 HRS, LOCAL STANDARD TIME

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO | .1730+001 | NO | .3694-002 | NO2 | .9154-001 | NMHC | .9761+000 |
| NONR | .5976-001 | ETH | .1124-001 | OLE | .3210-002 | PAR | .6432-001 |
| FORM | .2346-001 | ALD | .5093-001 | ARO | .7321-002 | TOL | .9595-002 |
| O3 | .1914+000 | HONO | .1215-003 | HNO3 | .4830-001 | PAN | .4454-002 |
| DCB1 | .6659-002 | DCB2 | .2452-002 | RNO3 | .3086-005 | H2O2 | .2869-004 |
| O | .4635-008 | O1D | .1351-014 | NO3 | .8188-005 | N2O5 | .2615-003 |
| HO | .8873-007 | HO2 | .9198-005 | HO4N | .2464-003 | RO | .9552-009 |
| RO2 | .4834-005 | RTO | .3970-010 | RXO | .1182-009 | FRO2 | .3638-006 |
| FRO | .6460-010 | R1O2 | .1325-005 | RTO2 | .1819-006 | RXO2 | .5428-006 |
| COOH | .1932-003 | | | | | | |

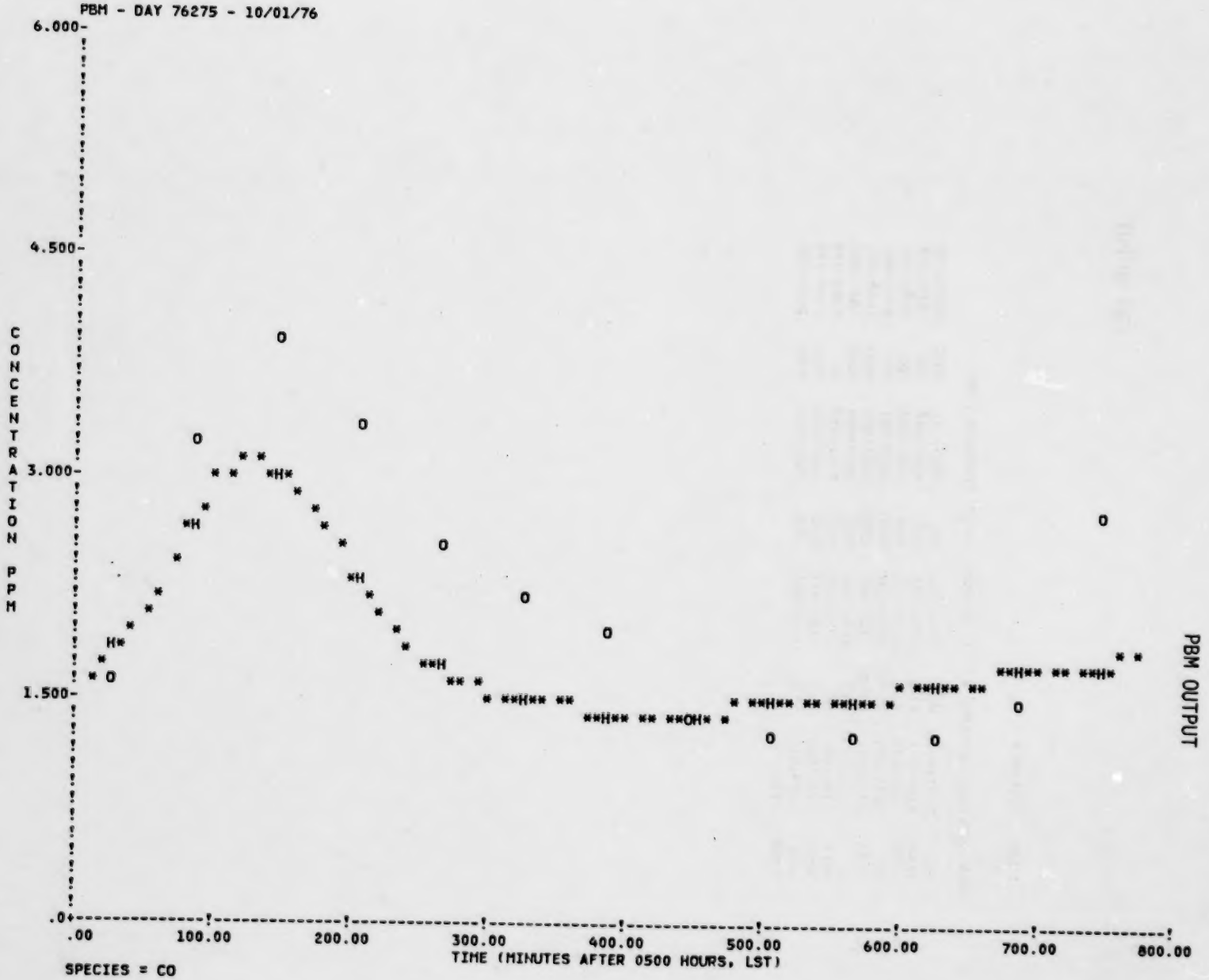
HOUR-AVERAGES CENTERED AT 16.50 HRS, LOCAL STANDARD TIME

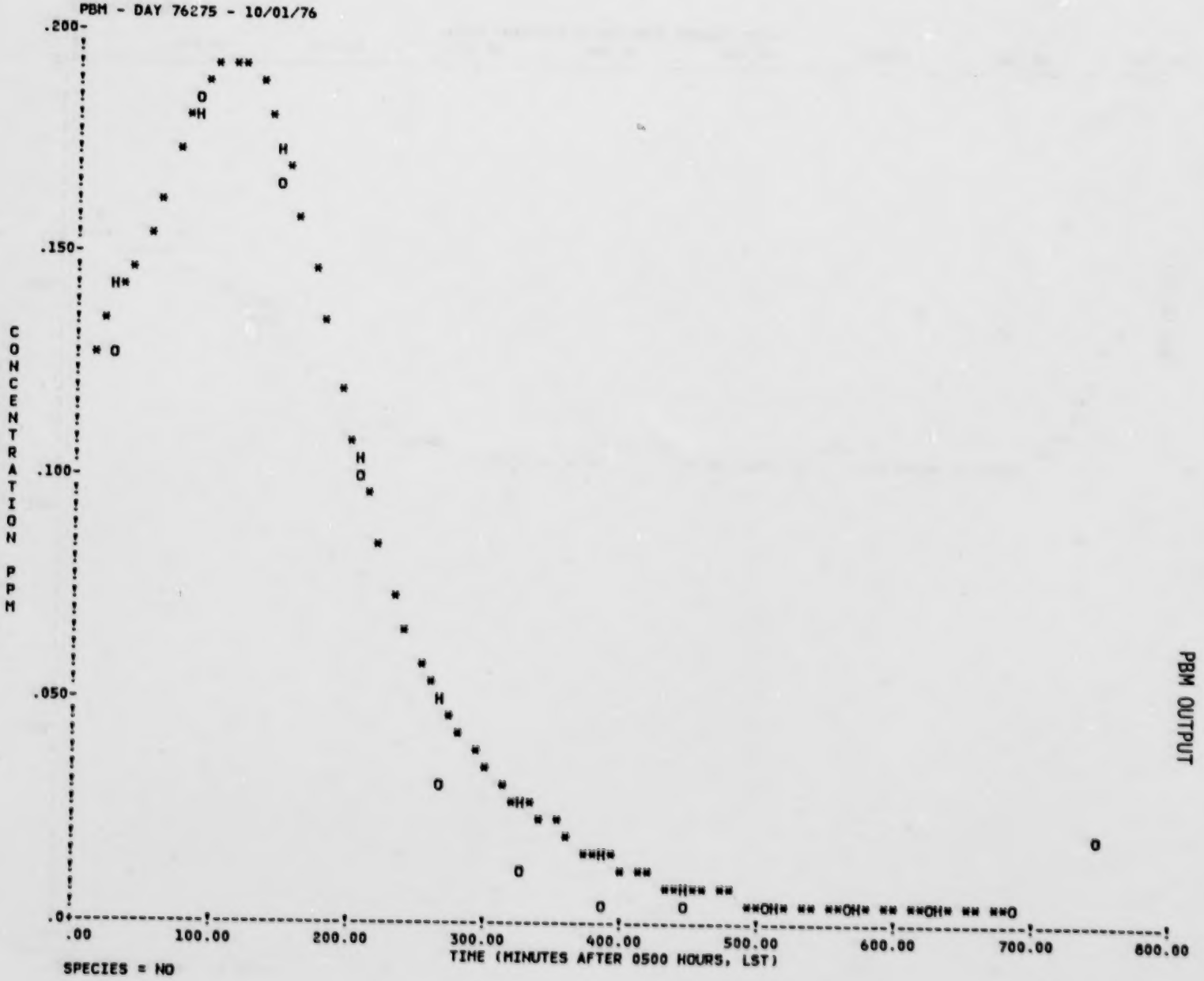
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO | .1816+001 | NO | .1849-002 | NO2 | .9121-001 | NMHC | .9913+000 |
| NONR | .6126-001 | ETH | .1196-001 | OLE | .3500-002 | PAR | .6563-001 |
| FORM | .2516-001 | ALD | .5152-001 | ARO | .7749-002 | TOL | .9780-002 |
| O3 | .1903+000 | HONO | .1688-003 | HNO3 | .5302-001 | PAN | .4975-002 |
| DCB1 | .6484-002 | DCB2 | .2442-002 | RNO3 | .3069-005 | H2O2 | .4678-004 |
| O | .2363-008 | O1D | .2973-015 | NO3 | .1526-004 | N2O5 | .5071-003 |
| HO | .5674-007 | HO2 | .1205-004 | HO4N | .3363-003 | RO | .6618-009 |
| RO2 | .6604-005 | RTO | .2592-010 | RXO | .8015-010 | FRO2 | .4745-006 |
| FRO | .4193-010 | R1O2 | .1409-005 | RTO2 | .2360-006 | RXO2 | .7313-006 |

COOH .2206-003

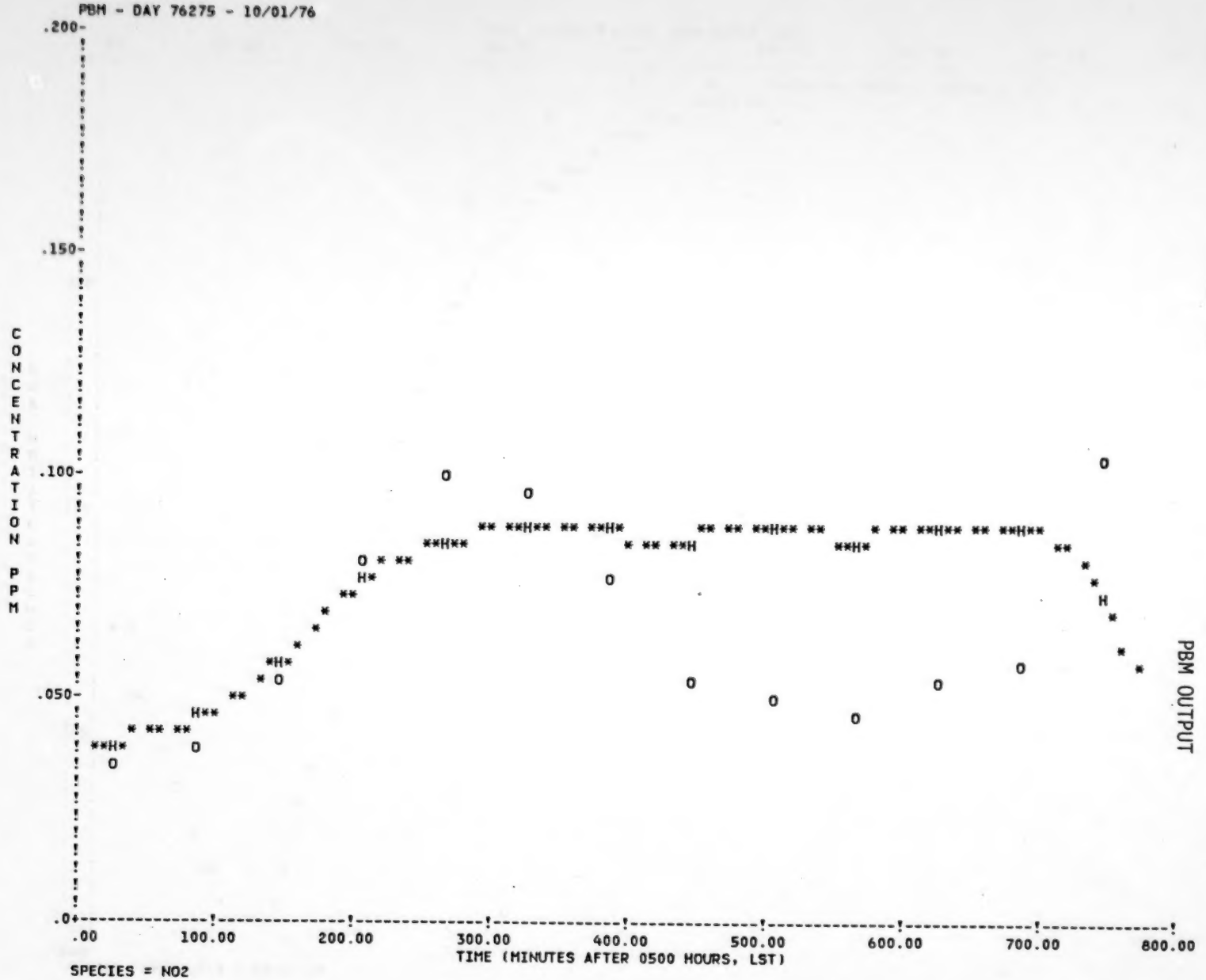
HOUR-AVERAGES CENTERED AT 17.50 HRS, LOCAL STANDARD TIME

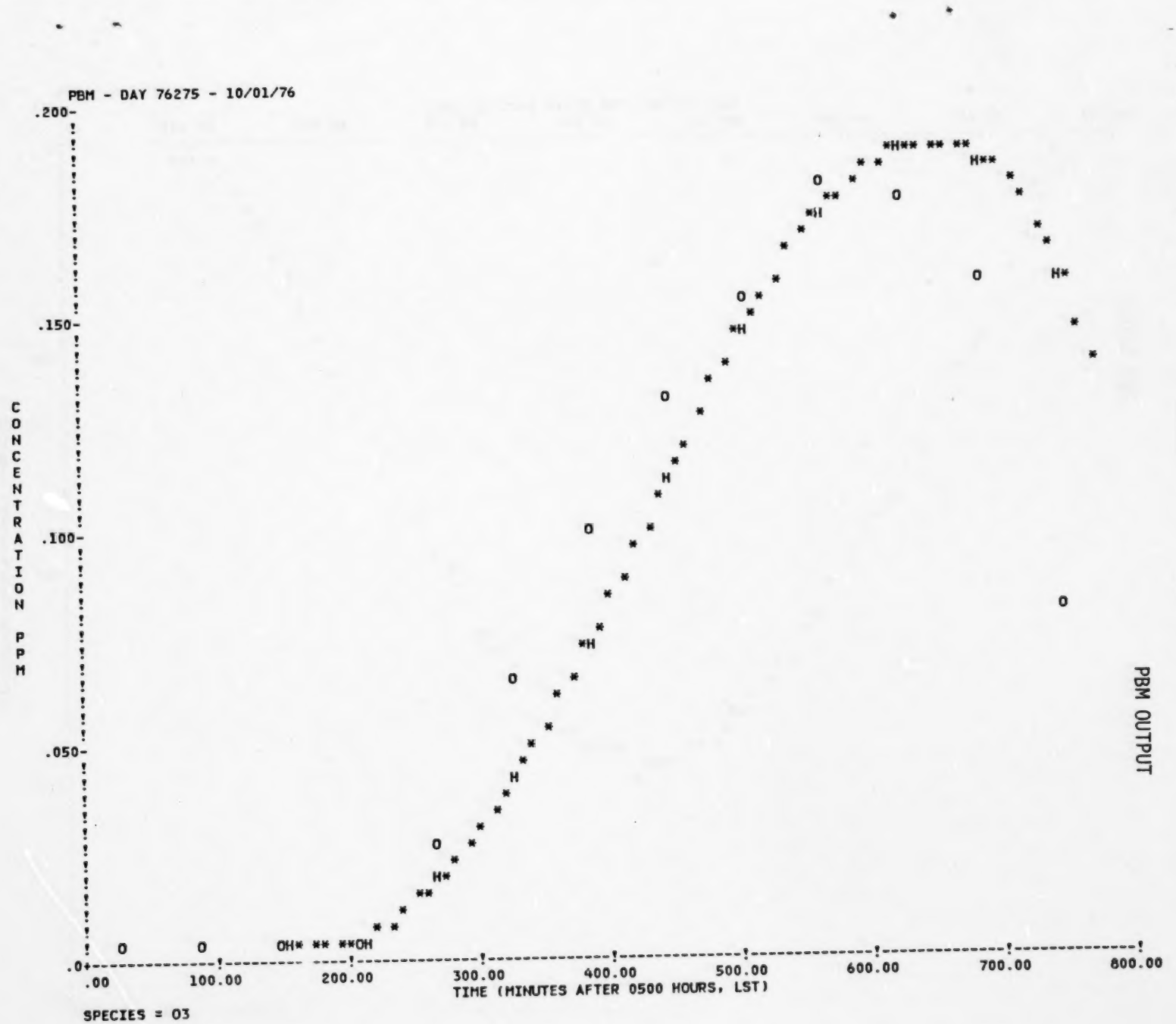
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO | .1893+001 | NO | .2656-003 | NO2 | .7554-001 | NMHC | .9867+000 |
| NONR | .6159-001 | ETH | .1281-001 | OLE | .4145-002 | PAR | .6621-001 |
| FORM | .2676-001 | ALD | .5045-001 | ARO | .8432-002 | TOL | .9976-002 |
| O3 | .1633+000 | HONO | .4298-003 | HNO3 | .6650-001 | PAN | .5391-002 |
| DCB1 | .6009-002 | DCB2 | .2338-002 | RNO3 | .2841-005 | H2O2 | .1468-003 |
| O | .2971-009 | O1D | .1564-016 | NO3 | .5679-004 | N2O5 | .1869-002 |
| HO | .1796-007 | HO2 | .3385-004 | HO4N | .9391-003 | RO | .3382-009 |
| RO2 | .4386-004 | RTO | .8187-011 | RXO | .2667-010 | FRO2 | .1975-005 |
| FRO | .1253-010 | R1O2 | .1419-005 | RTO2 | .7437-006 | RXO2 | .2483-005 |
| COOH | .2436-003 | | | | | | |

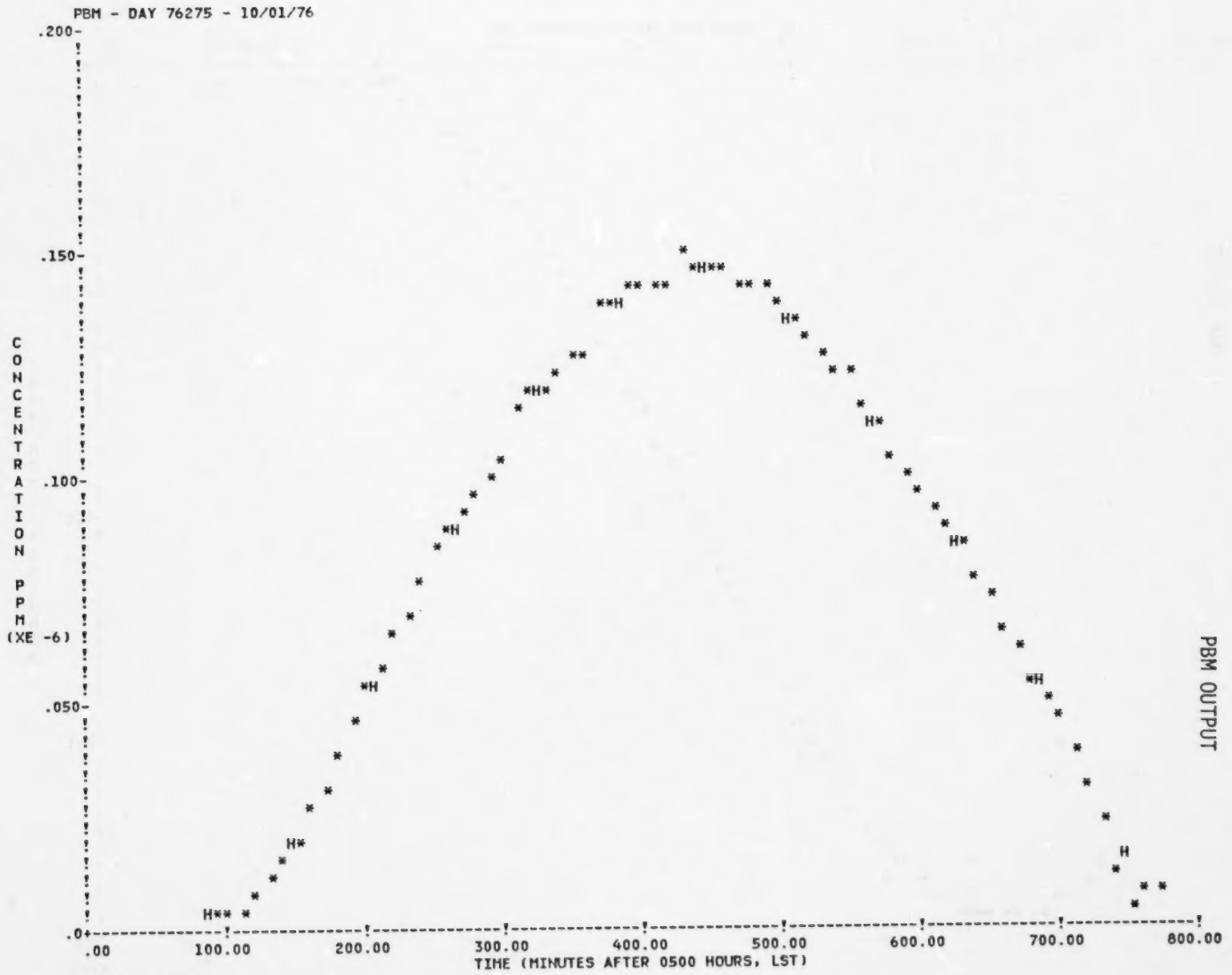

PBM - DAY 76275 - 10/01/76
6.000
4.500
3.000
1.500
.0
CONCENTRATION PPM
.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
800.00
TIME (MINUTES AFTER 0500 HOURS, LST)
SPECIES = CO
PBM OUTPUT


PBM - DAY 76275 - 10/01/76
.200
.150
.100
.050
.0
CONCENTRATION PPM
.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
800.00
TIME (MINUTES AFTER 0500 HOURS, LST)
SPECIES = NO

PBM OUTPUT


PBM - DAY 76275 - 10/01/76
.200
.150
.100
.050
.0
CONCENTRATION PPM
.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
800.00
TIME (MINUTES AFTER 0500 HOURS, LST)
SPECIES = NO2
PBM OUTPUT


PBM - DAY 76275 - 10/01/76
.200
.150
.100
.050
.0
CONCENTRATION PPM
.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
800.00
TIME (MINUTES AFTER 0500 HOURS, LST)
SPECIES = O3
PBM OUTPUT


PBM - DAY 76275 - 10/01/76
.200
.150
.100
.050
.0
CONCENTRATION PPM (XE -6)
.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
800.00
TIME (MINUTES AFTER 0500 HOURS, LST)
SPECIES = HO

PBM OUTPUT

## REFERENCES


Bucon, H. W., J. F. Macko, and H. J. Taback, 1978: Volatile organic compound (VOC) species data manual. EPA-450/3-78-119, U.S.EPA, Research Triangle Park, NC, 260 pp.

Demerjian, K. L. and K. L. Schere, 1979: Applications of a photochemical box model for $O_3$ air quality in Houston, Texas. Proceedings, Ozone/Oxidants: Interactions with the Total Environment II, Houston, TX, 14-17 Oct. 1979, APCA., Pittsburgh, PA, pp. 329-352.

Demerjian, K. L., K. L. Schere, and J. T. Peterson, 1980: Theoretical estimates of actinic (spherically integrated) flux and photolytic rate constants of atmospheric species in the lower troposphere. In Advances in Environmental Science and Technology - Vol. 10, J. N. Pitts et al., eds., John Wiley and Sons, New York, pp. 369-459.

EPA, 1977: User's manual for single-source (CRSTER) model. EPA-450/2-77-013, U.S.EPA, Research Triangle Park, NC.

Farrow, L. A. and D. Edelson, 1974: The steady-state approximation: fact or fiction? International Journal of Chemical Kinetics, 6, 787-800.

Gear, C. W., 1971: The automatic integration of ordinary differential equations. Communications of the ACM, 14, 176-179.

Holzworth, G. C., 1972: Mixing heights, wind speeds, and potential for urban air pollution throughout the contiguous United States. EPA Report AP-101, U.S.EPA, Research Triangle Park, NC.

Jones, F. L., R. W. Miksad, A. R. Laird, and P. Middleton, 1981: A simple method for estimating the influence of cloud cover on the $NO_2$ photolysis rate constant. Journal of the Air Pollution Control Association, 31, 42-45.

Lamb, R. G., 1983: A regional scale (1000 km) model of photochemical air pollution. Part 1. Theoretical formulation. EPA-600/3-83-035, U.S.-EPA, Research Triangle Park, NC.

McRae, G. J., J. A. Leone, and J. H. Seinfeld, 1983: Evaluation of chemical reaction mechanisms for photochemical smog. Part I - Mechanism descriptions and documentation. EPA-600/3-83-086 U.S.EPA, Research Triangle Park, NC.

NCC, 1970: Card Deck 144 WBAN - Hourly Surface Observations Reference Manual, National Climatic Center, Asheville, NC.

Schere, K. L. and K. L. Demerjian, 1977: A photochemical box model for urban air quality simulation. Conference proceedings, 4th Joint Conference on Sensing of Environmental Pollutants, New Orleans, LA, 7-11 Nov. 1977, ACS, Washington, DC, pp. 427-433.

Schere, K. L. and J. H. Shreffler, 1984: Examination of one-hour $NO_2$ predictions from photochemical air quality models. EPA-600/3-84-046, U.S.-EPA, Research Triangle Park, NC, 107 pp.

Schere, K. L. and J. H. Shreffler, 1982: Final evaluation of urban-scale photochemical air quality simulation models. EPA-600/3-82-094, U.S.-EPA, Research Triangle Park, NC, 259 pp.

Shreffler, J. H. and K. L. Schere, 1982: Evaluation of four urban-scale photochemical air quality simulation models. EPA-600/3-82-043, U.S.-EPA, Research Triangle Park, NC, 179 pp.

# APPENDIX A

## CONSIDERATIONS FOR USING ALTERNATIVE CHEMICAL KINETIC MECHANISMS

The default chemical kinetic mechanism included in the PBM system was developed by Dr. Kenneth Demerjian of the EPA. It simulates the urban photochemistry of the $O_3$-$NO_x$-HC reaction system and includes a temporal variation in the photolytic and temperature-dependent reaction rate constants. The Demerjian mechanism is one of several recognized photochemical smog mechanisms. Circumstances may exist where the user desires to employ an alternative chemical kinetic mechanism in the PBM system. This is relatively easy to do although the change may affect initial and boundary concentrations, emissions, and the diurnal variations in particular rate constants. It should not be attempted without the expert services of a chemist familiar with photochemical smog simulations and a computer programer familiar with simulation models. This appendix highlights the sections of code within the computer programs constituting the PBM system that may need revision if an alternative chemical kinetic mechanism is used and discusses effects on input data to the system. Line numbers referencing the computer programs are approximations and are intended only to guide the user to the general section of affected code.

### PBMMET

Although the meteorological preprocessor would not seem to deal directly with the PBM chemistry, it does generate diurnally varying rate constants for the 11 photolysis reactions in the default kinetic mechanism. If the alternative mechanism contains photolysis reactions different in structure or order of appearance from those in the default mechanism, the following changes are needed.

| In the main program PBMMET: | | Change Code*: |
|---|---|---|
| line 103 | COMMON Z(10),...,RTCON(10,10,7) | A |
| line 107 | .....PRC(110,11),ARC(110,11),CRT(27,10,7) | A,B |
| line 366 | DO 230 K=1,7 | A |
| line 373 | DO 250 K=1,11 | B |
| line 390 | DO 310 K=1,7 | A |
| line 438 | DO 350 K=1,11 | B |
| line 443 | DO 360 K=1,11 | B |
| line 485 | DO 440 K=1,11 | B |
| line 493 | DO 470 K=1,11 | B |
| line 499 | DO 490 K=1,11 | B |
| line 550 | WRITE (NOUT,2450) (ARC(I,K),... | B |
| line 551 | WRITE (NOUTD,2500) TIME(I),... | B |
| line 554 | DO 560 K=1,11 | B |
| line 556 | WRITE (NOUTD,2500) TIME(1),... | B |
| lines 414-417 | Delete these lines. They are specific to the photolysis reactions of the default chemical kinetic mechanism. | |

| In the subroutine BLKMET: | | |
|---|---|---|
| line 5 | COMMON Z(10),...,RTCON (10,10,7) | Change 7 to number of photolysis reactions with given clear-sky theoretical values if number is > 7. |

---

*A = Change 7 to number of photolysis reactions with given clear-sky theoretical values if number is > 7.

B = Change 11 to total number of photolysis reactions.

| | | |
|---|---|---|
| lines 11-112 | DATA ((RTCON)(I,J,1)),... | Update this data array corresponding to the clear-sky theoretical values of the photolytic rate constants for zenith angles (I) of values Z and altitudes (J) of values HTRT. Rate constant units are minute $^{-1}$. |

PBMAQE

The existing version of the air quality and emissions preprocessor is tied directly to the chemical species contained in the default chemical kinetic mechanism and will probably require a complete revision for a mechanism with different species, including different hydrocarbon reactivity classes. The purpose of this preprocessor is to set up data for the PBM for initial species concentrations, hourly lateral and top boundary species concentrations, hourly observed species concentrations, and hourly emissions. Most other mechanisms will include initial concentrations of CO, NO, and $NO_2$, but may differ in the reactivity splitting of the hydrocarbons. These splits should be consistent with the mechanism used. Boundary concentrations usually specify $O_3$ and may include precursor species as well. Emissions must include $NO_x$ and THC and must be divided into NO, $NO_2$, and the hydrocarbon reactivity classes by the preprocessing program. If CO is a species in the mechanism, CO emissions must also be specified.

PBM

The PBM has been constructed to optionally read in an alternative chemical kinetic mechanism. The subroutine ANALYZ is invoked to do this. This subroutine is linked or mapped into the final executable program only when a mechanism other than the default mechanism is used. Other required code changes are outlined below. The PBM has been set up to accommodate up to 50 reactive species, 5 additional inert species, and 75 individual chemical reactions. If any of these limits are exceeded in an alternative mechanism,

certain arrays in COMMON and DIMENSION must be expanded accordingly throughout the PBM. These arrays (and their current sizes) include:
NAME(55), YAX(55), ICODE(3,50), Y(8,50), SAVCON(100,50), KOBS(50), KPLOT(50), AVCON(18,50), ERROR(50), SUM(50), YMAX(50), PSAVE($50^2$), SAVE(12,50), RK(75), COEFF(3,75), NMPD(3,75), NMRC(4,75), KCOF(75,55), KPRD(3,75), KRCT(4,75), and KRXN(75,55). Some subroutines contain local arrays that also would need to be enlarged. They are not listed here, although they can be readily identified by the characteristic size of 50, 55, or 75.

In the subroutine SETUP:

line 325 CALL ANALYZ (LFLAG) Remove 'C' from column 1 of line 325
line 326 IF (LFLAG.GT.0) GO TO 900 Remove 'C' from column 1 of line 326

In the subroutine DIFFUN:

line 75 DATA NUMNO/2/, NUMNO2/3/, NUMO3/13/

Change this data statement to show the position numbers in the species list of NO, $NO_2$, and $O_3$.

lines 110-111 +SDCONC(INDEX,I) = (RK(1)*SDCONC(INDEX,K))...

Change 1 in RK(1) corresponding to the reaction number for $NO_2$-->NO+O, and change 3 in RK(3) corresponding to the reaction number for $NO+O_3$-->$NO_2+O_2$.

In the subroutine RKUPDT:

This subroutine calculates the temperature-dependent rate constants for particular reactions in the default mechanism. The subroutine would need to be rewritten for an alternative kinetic mechanism.

In the subroutine BLKDAT:

line 34 DATA NIN/5/, NOUT/6/,...

Change 37 to the number of reactive species and 41 to the total number of species, including inert species.

lines 37-42 DATA NAME/...

Change this data statement to show the names of the species in the mechanism.

lines 49-51 DATA DELTIM/...

Change the data in IPHO to the numbers of the photolysis reactions. Change the data in YAX to specify the initial concentrations of species that will not be specified in the input data to the PBM.

lines 55-67 Change the rate constant array RK to the appropriate reaction rate constants for the alternative kinetic mechanism. Rate constants that are temperature-dependent or are for photolysis reactions are calculated elsewhere and can be set to zero here.

line 73 DATA MAXPRD/3/,...

Change MAXRXN to the maximum allowable reaction number. Change NRXN to the exact number of reactions in the alternative kinetic mechanism.

For the subroutine ANALYZ:

This subroutine must be compiled and linked into the PBM system. It reads and analyzes the new kinetic mechanism. The individual reactions are read, one to a card image, after all other inputs have been read by the PBM. The format for this data set is shown in Table A-1.

TABLE A-1. PBM CARD TYPE 23 - REACTIONS (1 card for each reaction) (used with subroutine ANALYZ)

| Variable | Format | Description | Units |
|---|---|---|---|
| NMRC | 4(A4,1X) | Alphanumeric names of reactant species (maximum=4) Coefficients of reactant species are set equal to 1. | - |
| COEFF | F6.0 | Stoichiometric coefficient of product species. | - |
| NMPD | A4 | Alphanumeric name of product species. | - |

Note: A maximum of 3 COEFF,NMPD pairs may be specified on each card (i.e. 3(F6.0,A4)).

Date _____

Chief, Atmospheric Modeling Branch
Meteorology and Assessment Division (MD-80)
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

I would like to receive future revisions to the User's Guide for the Photochemical Box Model.

Name _____
Organization _____
_____
Address _____
City _____ State _____ Zip _____

Phone (Optional) (___) ____ - _____

Computer Characteristics (Optional):

Computer _____
Compiler _____
Operating System _____